

# Upgrading of Solvent Extracted Athabasca Bitumen by Membrane Ultrafiltration

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Solvent extraction processes have been tested extensively for the separation of bitumen from surface-mineable, oil-bearing deposits (Sparks and Meadus, 1979; Fedde and Zavada, 1983; Benson, 1971). The end result of these processes is a solution of bitumen in a hydrocarbon solvent, usually a light naphtha. The bitumen solution contains only minimal amounts of solids and water; but, because of the constraints of the solid-liquid separation and washing steps, the bitumen concentration in the produced solutions can be quite low (Karnofsky, 1979). Solvent must be separated from these solutions for recycle back to the extraction step of the process. This is usually accomplished by conventional techniques such as distillation, multiple-effect evaporation, or steam stripping. Sometimes a combination of these techniques is required (Karnofsky, 1979). As a result of the low bitumen content of the solutions, the energy and capital costs associated with solvent recycle can be substantial.

The use of membranes for nonaqueous liquid separations is a recent application of this developing technology. Several patents can be found describing processes for the recovery of solvent used in lube oil dewaxing (Bitter, 1985) or the regeneration of used automotive oils (Parc et al., 1975). A Japanese company has reported the development of several solvent-stable ultrafiltration membranes for the removal of solids from a number of solvents (Iwama and Kazuse, 1982). The use of spiral-wound polysulfone membranes for the recovery of pentane solvent used in heavy oil deasphalting has been described by an American firm (Kulkarni et al., 1986).

Membrane processing of bitumen solutions would be a less energy-intensive means of recovering naphtha solvent. In contrast to distillation, which requires the latent heat of vaporization to be input to the process, membrane processing only requires a modest amount of sensible heat and sufficient pumping energy to establish a transmembrane pressure differential. For naphtha removal, however, a membrane capable of separation at a molecular weight of approximately 200 ( $C_{12}$ ),

approaching the regime of reverse osmosis, would be required. A more typical ultrafiltration application is the reduction of contaminant concentrations by the removal of high-molecular-weight asphaltenes. A high quality membrane permeate could eliminate the need for coking this fraction of the bitumen or the coke produced when processing an upgraded bitumen would be lower in heavy metals content. This material could be suitable for use as electrode coke, providing a new and profitable market for this process by-product. The removal of heavy metals, sulfur and nitrogen from bitumen feedstocks would also benefit the downstream distillation and catalytic process.

## Experimental Studies

### *Solvent extraction*

The bitumen solutions used for testing in this work were obtained using a rotating extractor (Farnand et al., 1985). The unit is a laboratory-scale test device comprising a 25-cm-diameter, 40-cm-long rotating drum with a loss in weight screw feeder and a solids discharger-drainer, working in a countercurrent flow mode. The bitumen extract passes to a settler where coarse particles are removed and returned to the extractor via a cyclone. The clarified bitumen solution, overflowing from the settler, becomes the feed to the membrane separation process. For this test the oil sand was a medium-grade material from the Suncor lease in the Athabasca region of Alberta. The solvent was a bitumen-derived diluent naphtha. Compositions of the various streams are shown in Table 1.

For comparison purposes, the composition of the bitumen solution produced commercially by the hot water process (HWP) is also shown. A sample of this material was obtained from the Oil Sands Sample Bank at the Alberta Research Council in Edmonton. Both types of bitumen solution were tested with similar results. However, the longer runs possible with the larger quantity of HWP centrifuge plant bitumen solution makes the results obtained with this material more reliable. Consequently,

**Table 1. Composition of Process Streams**

<i>Oil Sand</i>		
Bitumen, wt./wt. %		10.9
Solids, wt./wt. %		85.0
Water, wt./wt. %		4.1
Fines, wt./wt. % <44 $\mu$ m		24.0
<i>Solvent</i>		
Boiling Range, °C		38–200
Paraffins, vol. %		57.5
Naphthenes, vol. %		33.0
Olefins, vol. %		0.0
Aromatics, vol. %		9.5
<i>Solution</i>	<i>Extract</i>	<i>HWP</i>
Bitumen, wt./wt. %	37.0	56.9
Naphtha, wt./wt. %	61.5	37.0
Water, wt./wt. %	<0.5	5.5
Solids, wt./wt. %	1.0	0.6

the data presented here are based on tests carried out with this more concentrated solution.

### Membrane formation

Laboratory cast polysulfone membranes were made from Union Carbide Udel P1700 (U) and Imperial Chemical Industries Victrex 200P (V). The polymers were dissolved in commercial-grade N-methyl pyrrolidinone (NMP) with polyvinyl pyrrolidone (PVP) as a pore-regulating additive. Casting dopes from these constituents were machine-cast under controlled conditions onto spun-bonded polyester (P). The nascent membranes were then gelled with ice water and extensively leached at room temperature. To prepare them for non-aqueous service, the membranes were solvent exchanged by successive washings under moderate pressure with commercial 95% ethanol, hexanes and mineral oil.

Commercial flat sheet membranes from De Danske Sukkerfabrikker (DDS) were also used. These included polyvinylidene fluoride (FS), Udel polysulfone (GR), and sulfonated polysulfone (GS) membranes with a 6,000 molecular weight cut-off.

### Membrane testing procedures

Batch experiments were performed using a plate and frame membrane device (DDS Lab Module 20). In aqueous service, this unit is capable of simultaneously evaluating as many as 20 pairs of membranes arranged in a series configuration. A support plate separates each pair of membranes, with flow passing across the membrane surfaces and permeate collecting in the internal channels of the plate. The membrane/support plate assemblies are separated by spacer plates which distribute the feed flow. Significant pressure drops, due to the combination of high feed viscosity and the narrow spacer plate flow passages, limited oil separation to ten membrane pairs. Each membrane pair provided 300 cm<sup>2</sup> of usable area.

A measured quantity of feed oil was placed in the feed tank at the start of the run. The feed pump was started and oil was delivered under pressure to the membrane device where it separated into permeate and concentrate. During an initial period of 2 to 3 hours, both permeate and concentrate were recycled to the feed tank. The oil temperature was controlled by adjusting the flow of steam to a heat exchanger. After the start-up period, permeate was collected separately while the

concentrate continued to recycle to the feed tank. The recirculating flow was generally five to ten times greater than the permeate flow.

As the composition of the material in the feed tank changed throughout the experiment, permeation rates (flux), feed and permeate analyses were determined at both the beginning and the end of the run. Recovery, as used in this paper, is defined as the percent of the original oil collected as permeate.

### Analytical measurements

Densities were determined with an Anton-Paar Model 602 density meter. Viscosity data were obtained at 20°C or other temperatures as noted using a HAAKE Rotovisco RV10 viscometer equipped with a CV100 measuring system and a Mooney-Ewart test cell. Molecular weight averages were obtained using a Perkin Elmer liquid chromatograph with an Ultrastaygel GPC column and UV detection at 254 nm. Nickel, vanadium, and sulfur were analyzed using standard X-ray fluorescence spectroscopy on raw samples and comparing the results with synthetic standards. Nitrogen results were obtained by the conventional Kjeldahl procedure.

### Discussion

Table 2 presents pure water fluxes and separation results for a solution of polyethylene glycol (PEG, molecular weight 6,000) in water for the membranes tested here. A direct relationship does not exist between membrane performance in aqueous and nonaqueous media. The upper limit of permeate molecular weight distribution, when in hydrocarbon service, is lower than indicated by aqueous characterization (Kutowy et al., 1985). The present results indicate that the effective molecular weight cut-off of these membranes in hydrocarbon service is 2,000 to 3,000. The hydrophobic membrane polymer will interact more strongly with oil than with water, leading to differences in transport mechanism and membrane porosity. Experiments with pure solvents suggest that swelling of the polymeric membrane in a hydrocarbon environment produces a tightening of the membrane pore structure and lower molecular weight cut-off (Hazlett et al., 1986).

Table 3 presents data obtained at two recovery levels for four membranes. All membranes tested gave similar performance in terms of contaminant removal, with the sulfur, nitrogen and heavy metals content of the permeated oil typically reduced by 50, 70 and 95%, respectively, when compared with the feed material.

Figure 1 illustrates the maximum difference of permeate molecular weight distribution for membranes used in this study.

**Table 2. Typical Characteristics of Membranes Used in This Work**

Membrane	Polymer (%)	Flux (kg/m <sup>2</sup> · d)	% Separation PEG 6,000
95VP	28	630	94
90VP	25	3,240	89
50VP	18	6,130	74
80UP	18	5,360	81
20VP	15	9,810	27
FS81	—	3,100	68
GR81	—	740	88
GS81	—	880	96

**Table 3. Results for Athabasca Bitumen with 37 Vol. % Naphtha Dilution at 0 % /46 % Recovery\***

	Feed	Permeate			
		GR81	90VP	80UP	20VP
API Gravity	28.3/22.3	52.2/43.9	---/39.4	49.2/42.5	47.8/40.8
Viscosity (mPa · s)	22/123 (35°C)	1.12/1.60	1.22/---	1.32/2.09	1.42/2.19
Avg. Mol. Wt.	802/891	400/438	416/453	443/466	467/479
Sulfur wt. %	3.28/3.88	1.29/1.54	1.32/1.87	1.37/1.75	1.48/1.82
Vanadium, ppm	102/126	2/2	2/3	2/2	4/4
Nickel, ppm	33/40	1/1	1/1	1/2	2/2
Nitrogen, kg/m <sup>3</sup>	14.7/19.0	2.0/2.8	4.4/2.9	2.2/3.0	2.5/3.4
Flux, kg/m <sup>2</sup> · d	---/---	63/30	17/6	161/40	113/24

\*Flow rate = 0.108/0.025 kg/s

Temperature = 35°C

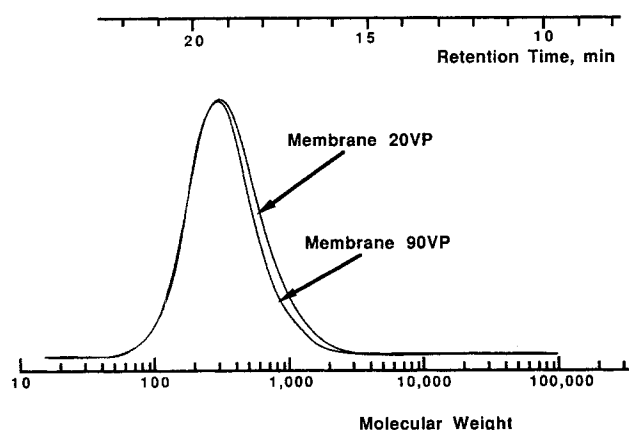
Inlet Pressure = 2.5 MPa

Outlet Pressure = 2.0 MPa

As can be seen, the curves are similar in shape with a slight shift toward higher molecular weight for the more open membrane (20VP). The key difference between the membrane formulations tested was the permeation flux. For example, GR81 and 90VP membranes gave similar separation results for PEG 6,000 in water, with the 90VP membrane having a higher pure water flux. When exposed to hydrocarbons, however, the more hydrophilic Victrex membrane, 90VP, displayed a lower flux than the hydrophobic Udel membrane, GR81. Membranes with a more open structure such as 80UP and 20VP have higher permeate fluxes but still give similar values for contaminant reduction. The slightly elevated levels of Ni and V for permeates from the Victrex 9.0VP membrane confirm the more open structure in this case.

As the separation proceeds, two effects serve to lower the permeation rates. The amount of permeable species present in the feed is lower and the feed viscosity rises, in the present case from 22 to 123 mPa · s. The change in viscosity limits the feed flow rate for a given inlet pressure and consequently the rate of mass transfer at the membrane surface is reduced. Feed temperature can be increased to compensate for this rise in viscosity.

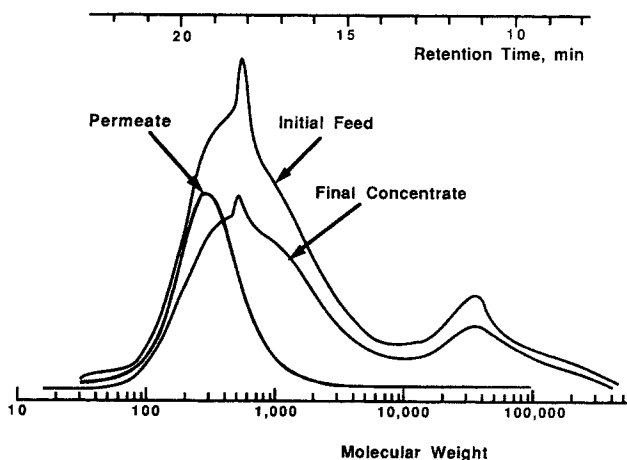
The feed sample, which was diluted with 37% naphtha, could easily be processed to a recovery of 46% at an acceptable flux.

**Figure 1. Permeate molecular weight distributions for membranes 90VP and 20VP.**

This indicates that the diluent does not permeate preferentially, but is recovered along with lighter oil components of the bitumen. This is a key difference between membrane separation and distillation. No optimization of the operating conditions or equipment configuration has been carried out. The experiment was stopped at 46% recovery as a result of pump limitations, not membrane performance.

As the processing proceeded, an almost crystalline-like solid precipitated out of the concentrated feed material. It appears that the asphaltene fraction becomes insolubilized when lighter oil components are removed. This is probably due to a shift in the aliphatic/aromatic balance of the concentrate (Mitchell and Speight, 1973). Proton and <sup>13</sup>C NMR analysis of the feed and permeate from two light crudes processed in the same fashion revealed a reduction in aromatic carbon content for the membrane permeates. The percentage reduction in aromatic protons is lower than that for the corresponding carbon content. This is consistent with removal of high-molecular-weight polyaromatic asphaltene material.

Figure 2 illustrates the molecular-weight distribution of initial feed, oil permeate and final concentrate for the 90VP membrane. The heights of the curves have been altered to allow

**Figure 2. Molecular weight distributions of initial feed, permeate and final concentrate for membrane 90VP.**

presentation of all three distributions on a single diagram. The absence of the asphaltene peak in the permeate is clearly seen. The 'blip' in the curves for the feed and concentrate at a molecular weight of 500 is believed to be due to a molecular species with sensitivity to 254 nm ultraviolet light.

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