Electronic Supplementary Material (ESI) for RSC Advances.

SUPPORTING INFORMATION FOR: Optimization of Closed–Cycle Oil Recovery: A Non–Thermal Process for Bitumen and Extra Heavy Oil Recovery

Pushpesh Sharma, Konstantinos Kostarelos, and Mohamad Salman

Experimental

The oil sand utilized in this study was acquired from Alberta Innovates Technology Futures, Alberta, Canada. Bitumen content of oil sand was quantified using the Soxhlet extraction with toluene as a solvent. The bitumen content was measured to be 12.8 wt.% on average. For characterization, bitumen was extracted with solvent extraction. The properties of the extracted bitumen are listed in Table SI-1.

Table SI-1: Properties of extracted bitumen

		SARA			
specific gravity	total acid number (mg of KOH/g of oil)	saturates (wt.%)	aromatics (wt.%)	resins (wt.%)	asphaltenes (wt.%)
0.977	2.94	23.85	28.21	15.13	32.81

The bitumen is thixotropic, displaying shear–thinning behavior at the higher shear rates (see Figure SI-1). In addition, bitumen viscosity decreases drastically with temperature increase. Bitumen viscosity at 10 s^{-1} shear rate is was measured for temperatures ranging from 10 to 50°C and exhibit an exponential decline shown in Figure SI-2. Note that the lower viscosity (573 cP) at the highest measured temperature (50°C) is still considered high with respect to oil recovery and poses microscopic and macroscopic displacement concerns if relying on a mobilization recovery mechanism. The C–COR approach does not rely on mobilization for recovery: nonetheless, bitumen viscosity is important with respect to the flow path of injected fluid and the microemulsion formed *in-situ*.

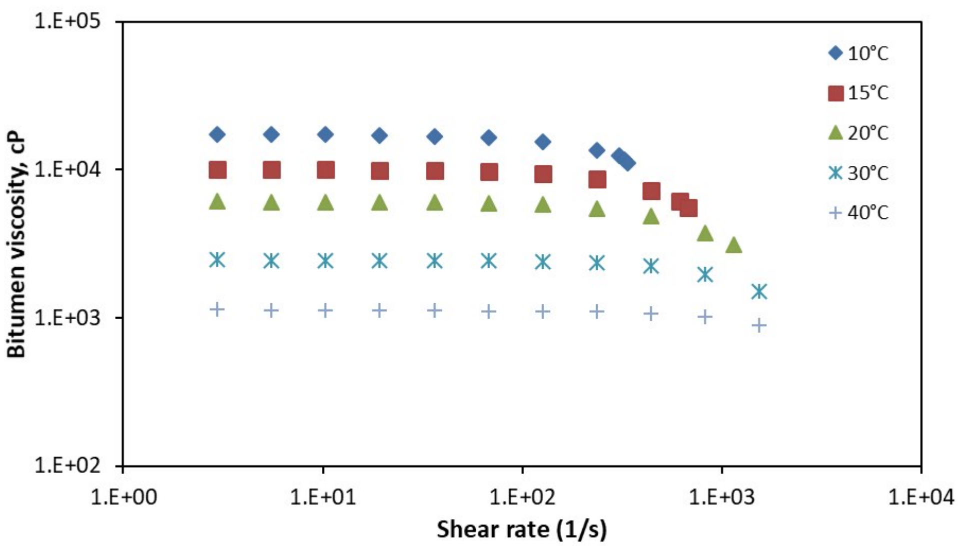

Figure SI-1: Bitumen viscosity at multiple temperature and shear rates; notice the shear thinning behavior at rates above 200 s^{-1}.

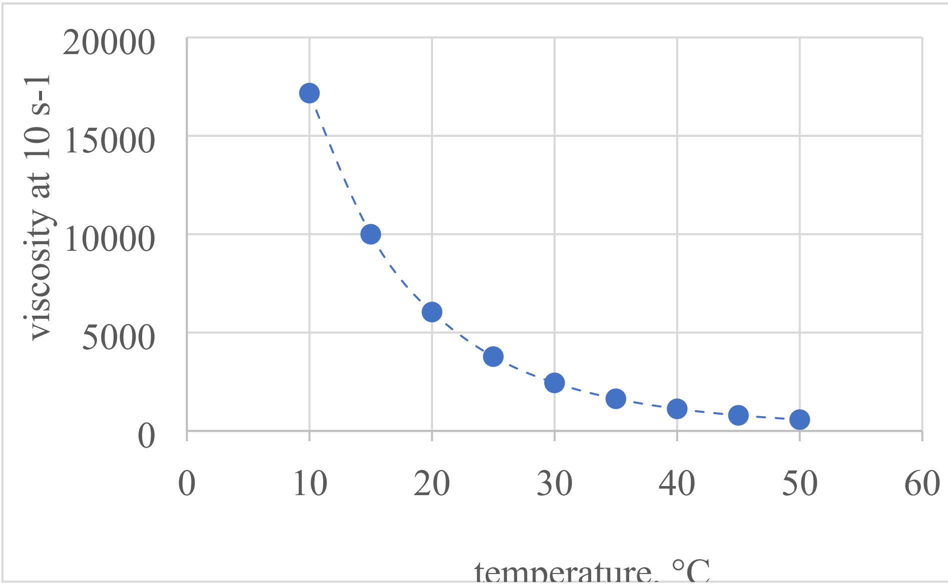

Figure SI-2: Exponential decline in bitumen viscosity measured at 10 s^{-1} shear rate as temperature increases.

The surfactants and co-surfactants used in the study are listed in Table SI-2. The details regarding the phase behavior studies to develop the formulation used for the present work are presented in Sharma *et al.*[1] Table SI-2 represents the selection after exploring over 20 surfactants and combinations of surfactants. Other chemicals supplied by various vendors as listed in Table SI-3.

Table SI-2: Surfactant types, vendors, and activities

trade name	surfactant type	vendor	activity (%)	MW* (Da)
Petrostep S13D HA	C13 13 PO alkoxy sulfate	Stepan	81.2	850
Petrostep S3B HA	C20-24 IOS	Stepan	57.9	450

*Estimated molecular weight.

Table SI-3: Laboratory grade chemicals and their vendors

chemical	vendor
sodium carbonate	VWR
2-butanol	Alfa Aesar
iso-propyl alcohol	Alfa Aesar
tri-ethylene glycol mono butyl ether (TEGMBE)	Alfa Aesar
sodium chloride	Sigma Aldrich
dichloromethane	Alfa Aesar
toluene	Alfa Aesar
hyamine (0.05M) titrant	Alfa Aesar
acetonitrile	VWR
ammonium acetate	VWR
A-5903 polymer	Kemira

Sample Analysis: Gas Chromatograph (GC) and Liquid Chromatograph (HPLC) analyses were used to measure oil content and surfactant content, respectively, in samples collected during each column test.

The GC or HPLC was calibrated before each column test and analyses were conducted in duplicate, where measurements that varied greater than 15% were repeated.

Static Tests

Solubilization tests were conducted in 20 ml glass tubes. Each tube was filled with 10 g of oil sand sample and 10 ml of the desired surfactant formulation was added to the tube. Tubes were sealed with aluminum foil and a plastic cap. Tubes were mixed gently and then allowed to equilibrate for 24 hours. After equilibration, the supernatant was collected and analyzed by GC/MS (Table SI-4). The formulation used for the adsorption tests was the basis for these tests: the formulation was varied with respect to the blend ratio of the two surfactants (IOS and sulfate), and two alternative co-solvents isopropyl alcohol and TEGMBE were studied as well. Sodium carbonate concentration was maintained at 4 wt.%. A control containing oil sand and only sodium carbonate was conducted and resulted in no oil solubilization.

Table SI-4: GC method for bitumen concentration measurement in micromeulsion

inlet temperature	250°C
column	He constant flow 1 ml/min
oven program	initial temperature 80°C for 1 min; ramp of 5°C per min to 275°C; hold up time 40 mins
front detector	300°C; hydrogen 30ml/min, air 350 ml/min
MS Quad	150°C
MS Source	230°C

HPLC methods used for surfactant analysis are unique to the surfactant type; the primary method utilized in this study is described in Table SI5.

Table SI-5: HPLC method for surfactant detection

injector	0.2 µL
solvent a	acetonitrile
solvent b	ammonium acetate 0.1 M
pump	1 ml/min
solvent ratio	initial: 1:1
	15 min: 9:1
	end: 9:1
column temperature	40°C
ELSD:	
evaporator	60°C
nebulizer	60°C
gas flow rate	1.6 SLM

Dynamic Tests (Flow experiments)

A photograph of the experimental setup and a flow diagram for the dynamic tests are shown in Figures SI-3 and SI-4, respectively. The setup employed an HPLC pump to deliver fluids at a constant rate or constant pressure. For all the column tests, the experiments were conducted using the same materials and procedures in order to provide comparable results. Multiple floating piston accumulators were prepared for various liquids (brine, surfactant formulations, etc.). The oil sand was packed into a Kimble Kontes Chromoflex glass column, 15 cm in length and 2.5 cm in diameter. A water circulator (ISOTEMP 6200) was used to maintain the required flow temperature. Omega PX-26 pressure transducers were used to measure pressure drop across the inlet and outlet. A vacuum pump was used to pull vacuum during measurements of the *bulk water fraction* (W_f). The bulk water fraction of the sand pack denotes the available pore volume for flow (Equation 1) and was measured in a similar manner as porosity for consolidated cores.

$$W_f = \frac{Pore\ Volume, PV - Oil\ Volume, V_{oil}}{Total\ Volume, V_{total}} \#1$$

Bulk water fraction is analogous to water saturation in the case of consolidated cores and monitoring the W_f provides a means of quantifying the oil recovery. Keeping in mind that oil sands are an unconsolidated media, the W_f increases as oil is recovered during the experiment. It is also important to keep in mind that the porosity is not known at the start of the flow experiments and, thus, bitumen content is not reported in terms of *saturation* but in terms of *mass content*. Thus, oil recovery can be assessed gravimetrically and using W_f, and both were used for confirmation of oil recovery for each column test.

Dynamic tests sand packs were prepared using Athabasca oil sand in the glass columns. The flow rate was maintained at 0.013 ml/min (0.27 m/day), vertically upwards, for each test except in Dynamic Test 4 where the rate was doubled. Experimental conditions are listed in Table SI-6. Microemulsion produced from these tests were collected in 12-ml glass tubes using a fraction collector.

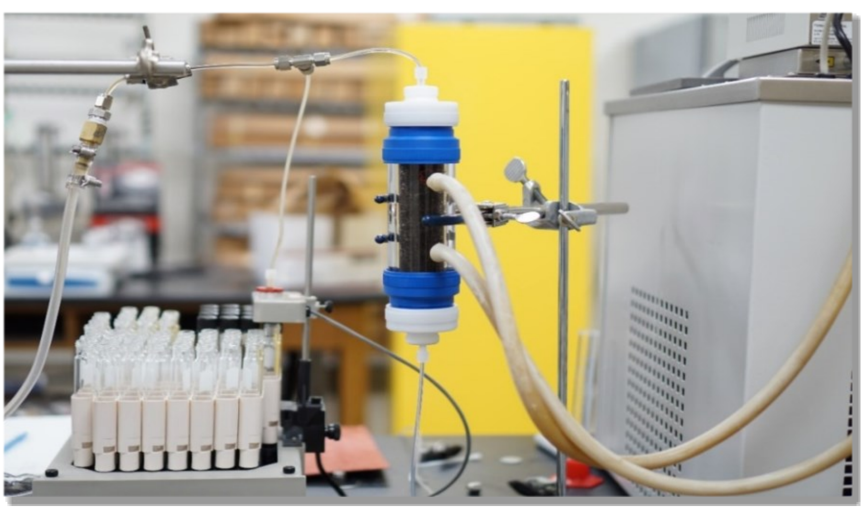

Figure SI-3: Experimental setup for dynamic tests where a jacketed column controlled the process temperature.

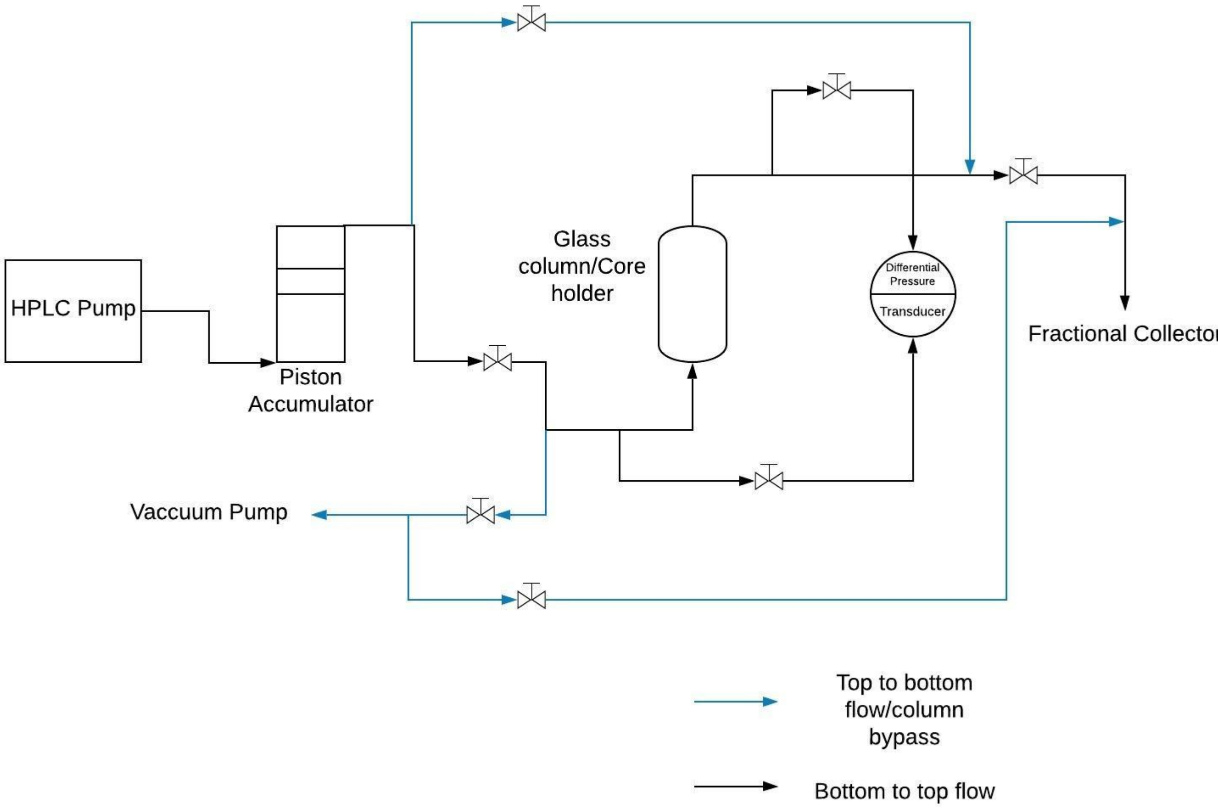

Figure SI-4: Flow diagram for the dynamic tests; blue–colored arrows highlight the bypass loop

Table SI-6: Dynamic test experimental conditions

test number	description	approach	temperature (°C)
1	baseline	continuous injection	20
2	elevated temperature	continuous injection	40
3	soaking	intermittent injection	20
4	high rate	continuous injection	20
5	polymer	continuous injection	20

Dynamic Test 1 was conducted at 20°C with the surfactant formulation based on static tests and treated as a baseline for optimization. Test 2 was performed with the same formulation but with thermal enhancement at 40°C and injection was stopped at 10,000 ppm bitumen concentration as noted above. Test 3 was conducted with a "soaking" injection scheme: one PV of the surfactant formulation was injected and the column was isolated for 13 hours (the same duration as the injection). This scheme was repeated until outlet concentration dropped below the stopping criteria of 10,000 ppm. Test 4 was designed to study the effect of flow rate on oil recovery and was conducted at the same conditions as the baseline (DT 1) but with a faster injection rate. As in the previous flow experiments and, for better comparison, the injection was stopped when outlet concentration fell below 10,000 ppm.

For Dynamic Test 5, the surfactant formulation was modified by adding 2000 ppm of A-5903 polymer solution. The stopping criterion of 10,000 ppm outlet concentration was not followed in this case because, in the presence of polymer, the GC method was not capable to properly compare the bitumen concentration level to stopping criteria and the test was continued longer than was likely needed.

After each dynamic test, a 1 wt.% NaCl solution was injected into the sand pack to remove all the remaining microemulsion remaining in the system. The bulk water fraction was re-measured after each test. The bulk water fraction change was used to calculate the mass of bitumen recovered and report the recovery of bitumen Equations 2 and 3).

$$\Delta PV = W_{f,final}V_{total} - W_{f,initial}V_{total} \#2$$

$$\%Recovery = \frac{(\Delta PV)\rho_{bitumen}}{bitumen\ weight} \times 100\#3$$

where $W_{f,initial}$ is bulk water fraction before the test, $W_{f,final}$ is bulk water fraction after the test, V_{total} is the total volume of the column, ΔPV is the change in pore volume due to bitumen recovery, ρ_{bitumen} is the density of bitumen.

Results and Discussion

Dynamic Tests

The properties of each sand pack measured prior to each dynamic test are listed in Table SI7. The sand pack mass includes the oil sand only, as received from the field. The mass of bitumen is calculated from the sand pack weight based on the average oil content measured of 12.8 wt.%. Note that the pore volume and permeability reported here are the initial values measured on the sand pack, where some of the pore space is occupied by immovable oil (bitumen) and these values will increase as oil is recovered.

Table SI-7: Sand pack properties measured prior to all dynamic tests

test	sand pack mass (g)	bitumen (g)	W_f initial (%)	pore volume initial (ml)	permeability initial (μm^2)	temperature (°C)
1	132.07	16.90	13.8	10.2	10	20
2	137.70	17.63	13.8	10.2	44	40
3	138.22	17.69	12.6	9.2	38	20
4	138.48	17.72	14.4	10.6	44	20
5	147.31	18.85	14.1	10.4	10	20

Dynamic Test 1. Figure SI-5 highlights the difference between sand samples at the outlet and inlet collected after terminating the experiment and emptying the sand from the column. It is clear that oil was recovered from the sand comparing photographs of the original oil sand to the photographs taken after the test was ended. Close examination of sand after the test also led to the conclusion that oil recovery at the inlet is better than the outlet.

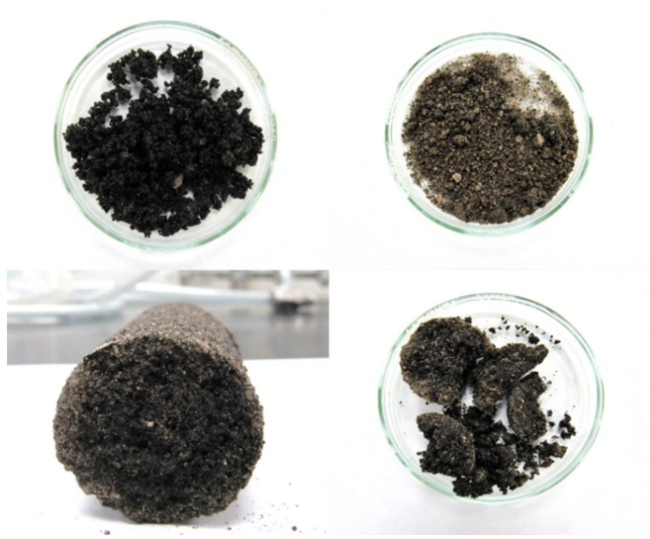

Figure SI-5:Dynamic Test 1 sand pack. Top left – original oil sand sample; top right – inlet sand sample after test; bottom left – end view of outlet sand sample after test; bottom right – outlet sand sample after the test.

Dynamic Test 5. The final test was conducted using a viscosifer to improve the macroscopic sweep efficiency or conformance. The surfactant formulation viscosity was 2.2 cP at 20°C without polymer. Surfactant formulations were prepared with a range of polymer concentrations and the viscosities measured at 20, 40, and 60°C, over a range of shear rates. The results of viscosity at 20°C and 1 sec^{-1} shear rate are listed in Table SI8.

Table SI-8: Polymer solution viscosity over a range of concentrations (20°C, 1 sec^{-1} shear rate)

polymer concentration (ppm)	viscosity (cP)
0	2.2
2000	18.8
4000	85.6
6000	238.2
10000	832.0

References for Supplemental Information

1. Sharma, P.; Kostarelos, K.; Lenschow, S.; Christensen, A.; de Blanc, P. C., Surfactant flooding makes a comeback: Results of a full-scale, field implementation to recover mobilized NAPL. *Journal of Contaminant Hydrology* **2020,** *230*.