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Fouling of Some Canadian Crude Oils

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ABSTRACT

A thermal fouling study was undertaken using three sour Canadian crude oils. Experiments were carried out in a re-circulation fouling loop, equipped with an annular (HTRI) electrically heated probe. Fluids at pressures of about 1000-1340 kPa under a nitrogen atmosphere were re-circulated at a velocity of 0.75 m/s for periods of 48 hours, and the decline in heat transfer coefficient followed under conditions of constant heat flux. Bulk temperatures were varied over the range 200-285°C, and initial surface temperatures from 300 to 380°C. Heat fluxes were in the range of 265-485 kW/m^2.

Surface temperature effects on fouling of the three oils were compared, and fouling activation energies estimated. For the lightest oil, a more detailed study of velocity, and bulk and surface temperature effects was carried out. Fouling rate decreased slightly with increasing velocity. Fouling rate increased with both surface and bulk temperatures; a rough correlation was developed using a modified film temperature weighted more heavily on the surface temperature. Deposits showed high concentrations of sulphur and of minerals, indicating the importance of iron sulphide deposition.

INTRODUCTION

Fouling in crude oil pre-heat trains is costly in terms of energy, maintenance and lost production. Although crude oil fouling has been a subject of much study [1-3], there are few investigations of fouling under controlled conditions which give guidance on predicting fouling rates for different oils under non-coking conditions.

Reported causes of fouling from crude oils include

i) impurities such as water, rust and other particulates
ii) gum or polymeric species formed through oxidation of reactive species in the oils
iii) insoluble asphaltenes from self-incompatible oils or from blending
iv) iron sulphide formation
v) coke formation due to reactions of polar fractions

These factors (i) to (v) become progressively more important as the oil temperature is raised- i.e., factor (i) can predominate at lower temperatures in the preheat train, whereas factors (iv) and (v) become more important near the furnace inlet temperature.

This research focused on three Canadian crude oils, all of which have significant sulphur content. For two of the oils, only a few results are reported, whereas the other oil was subject to more extensive study.

MATERIALS

Properties of the three oils are listed in Table 1. Cold Lake crude arises from heavy oil production, and is high in C_7 asphaltene content (8.6 %), and is substantially higher in viscosity, and in organic sulphur content (3.7 %) than the other two oils. Midale, has properties intermediate between those of Cold Lake and Light Sour Blend, with asphaltenes of 5%, and sulphur of 2.5%. Light Sour Blend has a viscosity a factor of 13 below that of Cold Lake, asphaltenes of 2 %, and a sulphur content of 1.3%. Oils were provided by Shell Canada Ltd.

The oils were characterized [4] using the Automated Flocculation Titrimeter (AFT), to determine the insolubility number (I_N) and the solubility blending number S_{BN} [5]. The results are listed below in Table 2. Viscosity at the film temperature was estimated using several methods [6-8], and the value from [8] which was close to the average prediction was used.

APPARATUS

A fouling loop was constructed for this research which could operate at pressures to 2 MPa, and at bulk temperatures of up to 285 °C. The feed tank (Fig. 1) has a capacity of 7.5-L of oil, and is equipped with external band heaters.

Table 1 Bench mark crude analytical data. (as supplied by Shell Canada Limited)

S.No	Analysis	CLK	MDL	LSB
1	Density @ 15 °C (gm/cc)	0.9582	0.8994	0.8534
2	Viscosity@ 25 °C (mPa-s)	157.80	27.26	12.74
3	Viscosity@ 6 °C (mPa-s)	566.20	113.50	161.70
4	"C_5 Asphaltenes Shell Method" (wt %)	13.20	6.44	3.13
5	"C_7 Asphaltenes (ASTM D3279-97)" (wt %)	8.58	5.05	2.05
6	Carbon Residues (wt %)	10.60	6.49	3.56
7	Ash (wt %)	0.036	0.003	0.003
8	Toluene Insolubles (%)	0.09	0.06	0.06
9	"Hot Filtration (ASTM D4870)" (%)	0.03	0.02	< 0.01
10	Organic Sulfur (ppm)	36750	24580	12600
11	Nickel (ppm)	66	18	7
12	Vanadium (ppm)	157	30	10
13	Calcium (mEq/L)	2	< 1	< 1
14	Sodium (mEq/L)	15	1	< 1
15	Iron (ppm)	4	< 1	< 1
16	Aluminium (ppm)	< 5	< 5	< 5
17	Zinc (ppm)	< 1	< 1	< 1
18	Copper (ppm)	< 1	< 1	< 1
19	Filterable Solids (wt %)	0.07	0.15	0.05
20	Centrifugal Solids (BS&W (v %))	0.35	0.1	< 0.025
21	API Gravity 15 °C	16.17	25.83	34.31

Table 2 Oil Compatibility Measurements.

Crude	Pa	Po	P	I_N	S_{BN}	δ_{oil} (Mpa$^{0.5}$)	δ_f (Mpa$^{0.5}$)
MDL	0.6102	0.8442	2.1655	38.5	75.0	17.53	16.40
LSB	0.6420	0.6523	1.8219	36.1	64.2	17.19	16.32
CLK	0.6817	0.7105	2.2324	31.4	64.3	17.19	16.17

Temperature control is maintained through a heated secondary surge vessel. A roto-gear positive displacement pump circulates the fluid at a pressure limited to 1.25 MPa by the packing in the pump. Flow was measured by an orifice plate.

An annular test section was used, with an HTRI-type probe of 1.065 cm outside diameter supplied by Ashland Chemical, Drew Division. The annulus was fabricated from Type 316 stainless steel pipe with an inside diameter of 1.585 cm.

The heat flow was calculated from measured voltage and current readings, and the over all heat transfer coefficient calculated by:

$$U = Q / (A \cdot \Delta T) \qquad (1)$$

Pressure in the loop was maintained manually using nitrogen which was bled into the system during initial heating of the oil. After experiments, the probe was removed for mechanical deposit recovery and chemical cleaning. The loop was then drained, purged with nitrogen, cleaned with Varsol at 75°C, and re-purged.

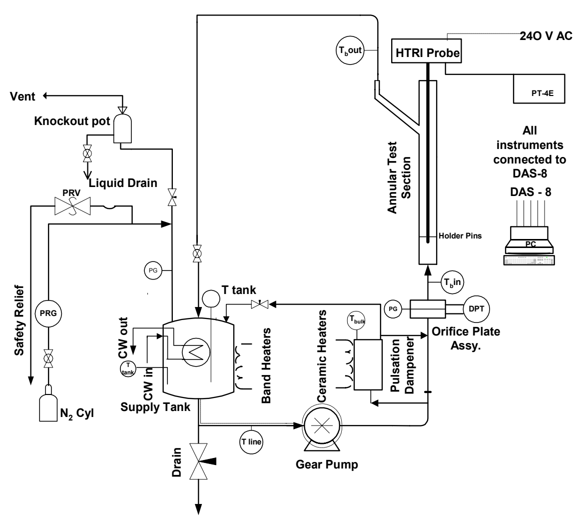

Fig. 1 Schematic diagram of the fouling loop.

RESULTS AND DISCUSSION

Fouling Tests with the Three Oils

For comparisons of fouling characteristics of the three crude oils, experiments were carried out at bulk temperatures of 210-275 °C, and surface temperatures about 100 °C higher. Velocity was set at 0.75 m/s. Due to the marked difference in viscosity, Reynolds numbers were much lower for the Cold Lake crude.

Figures 2 a-c show results from typical fouling experiments, which lasted about 2 days. For LSB (Fig. 2a), after an initial unsteady period which lasted about 3 hours, the overall heat transfer coefficient remained constant at 4.56 kW/m^2K for another six hours. It then declined approximately linearly with time by about 20 % over the final 45 hours of the run. The surface temperature increased by some 22°C from its initial value of 350°C. Bulk temperature remained constant.

Results for Midale crude are shown in Fig. 2b. There is no induction period observed after the initial unsteady state period. The overall heat transfer coefficient decreased by 27% in two stages, with more rapid fouling for the first nine hours than for the remaining 42 hours. For this run, the fouling rate was taken over the second stage, which had the longer time period. The heaviest crude oil, Cold Lake, had the lowest initial heat transfer coefficient, as shown in Fig. 2c. A 4-5 hour induction period preceded an 18 % decline in heat transfer coefficient over the duration of the run.

The value of the clean coefficient was calculated from ten data points taken over the time period 2.5 to 3.5 hours. The fouling resistance was then determined as

$$R_f = 1/U - 1/U_o \qquad (2)$$

and the fouling rate calculated from the slope of the linear plot of 1/U versus time, after any induction period. This rate was therefore calculated over some 30-40 hours of each run.

At the end of each experiment the viscosity was determined. Typically it doubled over the run due to a combination of preferential loss of lighter components of the crude and possible degradation. Calculations show that this viscosity change may have caused a decrease in heat transfer coefficient of about 5%, leading to an over estimation of fouling rates in this work.

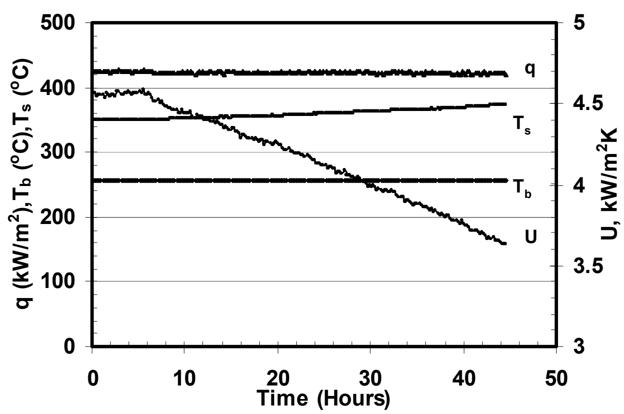

Fig. 2a Overall parameter plot of fouling for LSB crude oil (Re_b 5000)

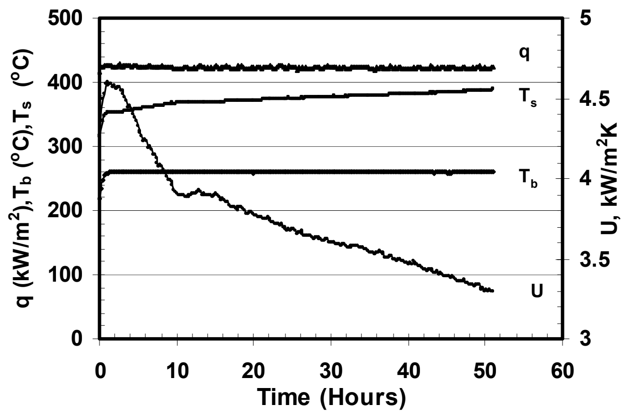

Fig. 2b Overall parameter plot of fouling for MDL crude oil. (Re_b 3300)

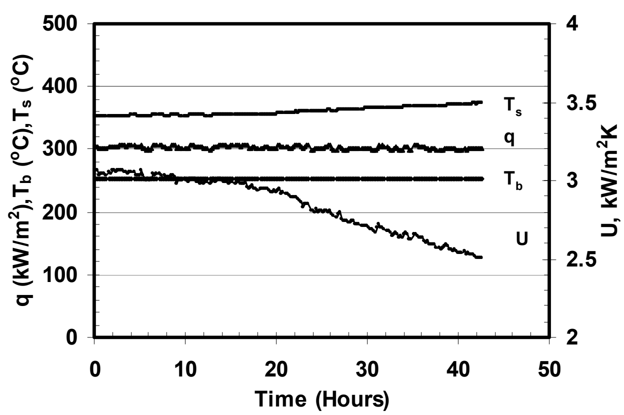

Fig. 2c Overall parameter plot of fouling for CLK crude oil (Re_b 1200)

Figures 3a and 3b show photographs of fouled probe from the LSB oil. Generally the rough black deposits were limited to the heated section of the probe.

Fig. 3a Photograph of the probe with deposits (showing the clean surface at the inlet and outlet of the heated test section) after an LSB run.

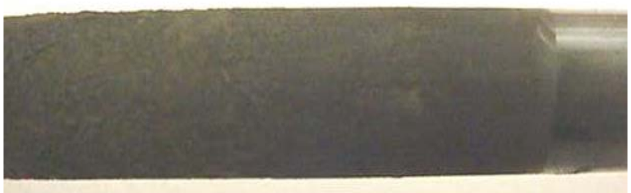

Fig. 3b Photograph of the probe with deposits focused at the mid-section of the heated test section.

Figure 4 shows R_f versus time data for three runs carried out with LSB crude oil, to check reproducibility of the results. The three runs were carried out at near identical conditions.

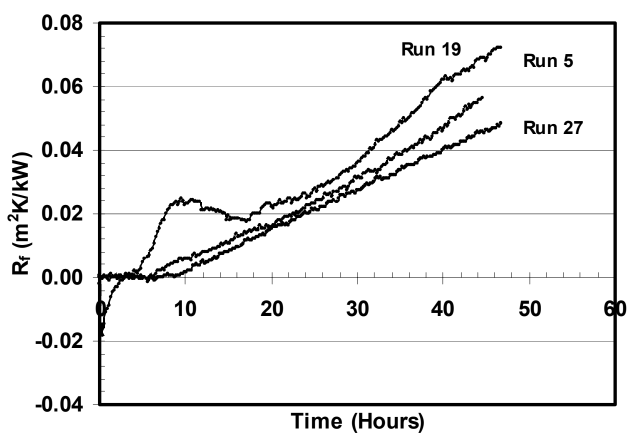

Fig. 4 Reproducibility of LSB crude oil fouling runs.

As shown in Table 3, reproducibility of fouling rates was reasonable, with a standard deviation of 8 % of the mean value.

Table 3 Tests of reproducibility of LSB crude oil fouling rates.

Parameters	Mean	Standard Deviation
T_f' (^oC)	324	1.58
Fouling Rate 10^{-7}.(m^2K/kJ)	3.86	0.33

Figure 5 is a semi-log plot of the fouling rate versus the inverse of the film temperature for the three oils tested. Although there is considerable scatter, the Cold Lake crude oil, which is highest in both sulphur and asphaltene content appears to have the highest fouling rate, followed by Light Sour Blend and Midale, whose fouling rates are quite similar. The fouling rates for all the oils are within a factor of two at film temperatures of 300-330°C. At a film temperature of 310˚C, the fouling rates are 9E-07 m^2K/kJ for CLK, and one half that for MDL and LSB. Although the velocity was the same for each, at 0.75 m/s, the film Reynolds numbers were respectively 1400, 3700 and 5600 for CLK ,MDL and LSB.

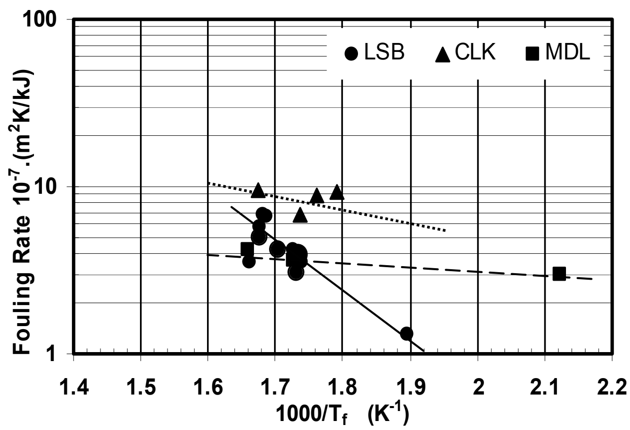

Fig. 5 Semi-log plot of fouling rate vs inverse of conventional film temperature for all the crude oils tested.

Effect of Bulk, Surface and Film Temperature

Experiments were carried out using LSB crude oil to investigate the effects of bulk and surface temperature on fouling. An objective of these experiments was to determine whether a single film temperature can correlate the rate of fouling, or whether both bulk and surface temperature effects must be accounted for separately. Figure 6a shows a fouling Arrhenius plot of rate versus inverse bulk temperature for a clean surface temperature of 357 ± 7°C, and bulk temperatures varying from 248 to 280°C. With a fixed surface temperature, increases in bulk temperature result in a rising film temperature. Fouling increased strongly with bulk temperature, yielding a fouling activation energy of 48.6 kJ/mol, which corresponded to a doubling of fouling rate with a 30°C increase in bulk temperature. The fouling activation energy can reflect transport, chemical reactions, and adhesion steps which may contribute to the rate of the overall process.

Figure 6b shows results of experiments carried out at a fixed bulk temperature of 275˚C, and surface temperatures varying from 335 to 370°C. Fouling rates increased sharply with initial surface temperature, doubling over an increase in surface temperature of approximately 40°C, with a fouling activation energy of 54.2 kJ/mol.

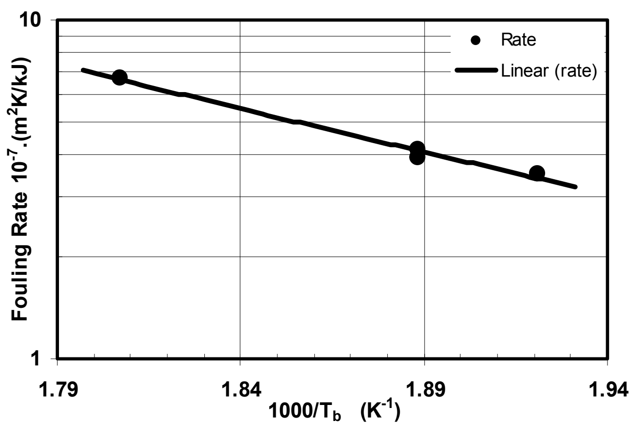

Fig 6a. Semi-log plot of fouling rate vs inverse of bulk temperature for LSB crude oil ($T_{s,o}$ ~ 357ºC).

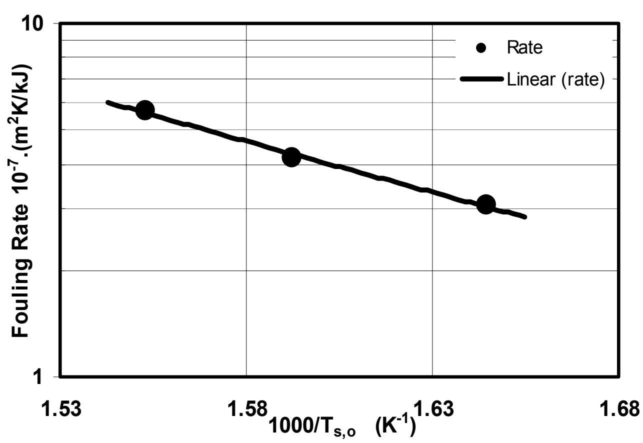

Fig 6b. Semi-log plot of fouling rate vs inverse of initial surface temperature for LSB crude (T_b ~ 275ºC).

Data from Fig. 6a and Fig. 6b, along with points from a few other experiments are shown in Fig. 7a, where rates are plotted versus film temperature,

$$T_f = 0.5\ T_b + 0.5\ T_{s,o} \qquad (3)$$

All the data do not collapse onto a single line. As shown in Fig. 7b, a slightly improved correlation was found by using a stronger weighting for the surface temperature,

$$T_f' = 0.3\ T_b + 0.7\ T_{s,o} \qquad (4)$$

The fouling activation energy for this correlation is 77.2 kJ/mol.

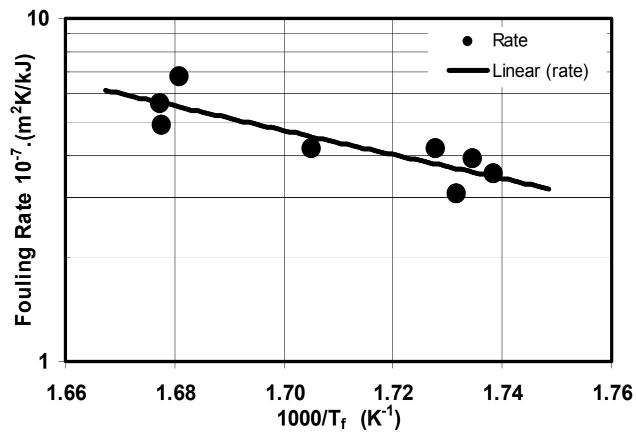

Fig. 7a Semi-log plot of fouling rate vs inverse of conventional film temperature for LSB crude oil.

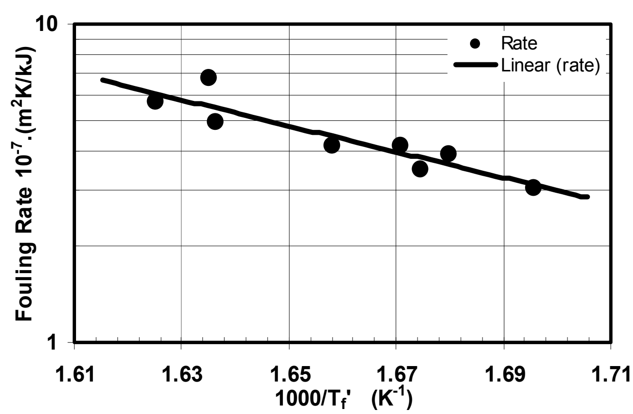

Fig. 7b Semi-log plot of fouling rate for LSB crude oil vs inverse of modified film temperature.

Velocity Effects

Experiments for velocity effects had to be carried out at lower velocities than the 0.75 m/s used in the above tests, since the power of the probe was limited. Experiments were therefore carried out at two lower velocities, where initial surface and bulk temperatures were held constant. Results in Figure 8 show a decrease in fouling rate as the velocity was increased.

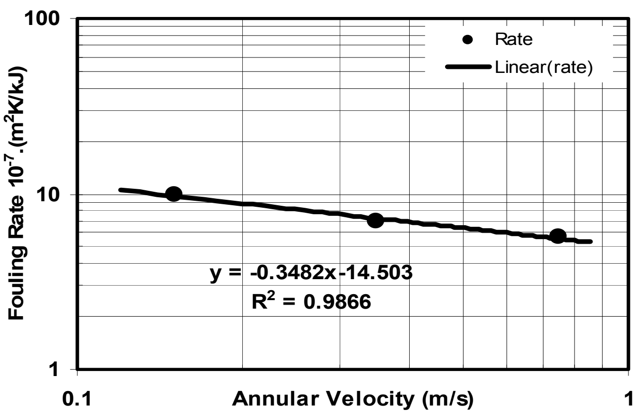

Fig. 8 Log-Log plot of fouling rate vs annular velocity for velocity dependence of fouling rate for LSB crude oil.

Fouling rate is seen to vary as velocity to the – 0.35 power. The values of calculated film Reynolds numbers for these experiments, based on extrapolated viscosity data, are within the range of 1100-5600 (Re_b 1000 -5000). The low velocity exponent in the current work is no doubt influenced by the flow regime. Panchal et al. [3], report a velocity dependence of –0.66 for the threshold model, for flow conditions which were turbulent.

Correlation of Results

The results of this study for LSB oil can be summarized in equation (5), which was found to fit the rate data within ± 8 %.

$$dR_f / dt = a. V^{-0.35}. \exp (- E_f / RT_f') \qquad (5)$$

As shown in Figure 9, the data incorporates ten runs for LSB crude oil, which yielded a fouling activation energy of 59.3 kJ/mol and the constant a = 0.05, where velocity is in m/s. Over the range tested, a 27°C increase in film temperature results in a doubling of the fouling rate.

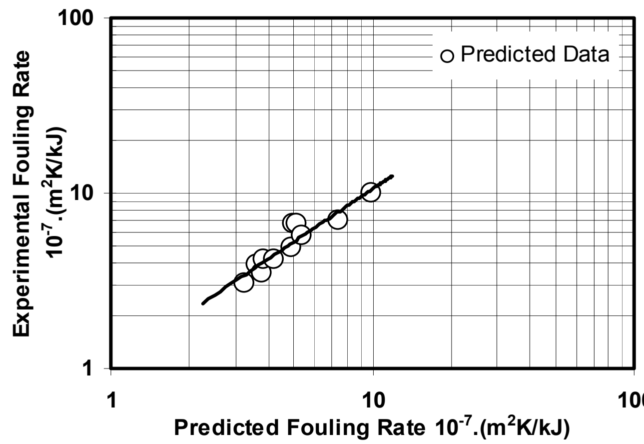

Fig. 9 Log-Log plot of experimental fouling rate vs predicted fouling rate (from Eq. 5) for LSB crude oil.

Deposit Analysis

Deposits were analysed using energy dispersive x-ray, giving point analyses on the deposit surface, and micro-elemental analysis for bulk content of C, H, S and N. Thermogravimetry was used to determine bulk ash content.

Results are shown in Table 4. Both inorganic matter and sulphur contents in the deposits were very high.. Sulphur can be present in either organic or inorganic forms, and hence a portion of the sulphur content appears in the ash analysis.

For LSB, ash content varied from 50-84%, and averaged 67 %. The organic portion of the deposit had an average H/C atomic ratio of 0.8. Sulphur content averaged 18.4 %, and appeared from the EDX data to be linked to iron content. On average for LSB deposits, Fe/S mass ratios were 2.2-2.5, which is significantly higher than the Fe/S mass ratio of 1.745 for pure FeS. For CLK, deposits ranged from 18-61 % ash, with H/C 0.83, and S content of 6-18 %. Fe/S by EDX was 1.97-2.0. For MDL, the two deposits analyzed had ash content of 44 and 80%, with corresponding C contents of 9.4 and 23 %. H/C atomic ratio was 0.9. From EDX measurements, the Fe/S mass ratio is 1.6-1.8. Thus, deposits from Midale oil have Fe/S ratios consistent with

FeS, whereas deposits from the other oils appear iron-rich, with Fe/S ratios greater than that of FeS. A rough correlation of decreasing ash content in the deposits with increasing film temperature is evident for LSB and CLK in Figure 10, which indicates the tendency for greater contributions from organic fouling at higher temperatures.

Table 4 Analyses of Deposits from the Three Crudes Tested.

Oil	% Ash	% C	% H	% N	% S	% Fe* (C-f)	% S* (C-f)	Fe/S* (wt/wt)
LSB	71.6	17.0	1.2	0.34	17.8	56.5	25.3	2.2
LSB	84.3	4.5	0.7	0.30	22.1	N/A	N/A	N/A
LSB	57.2	35.2	1.5	0.53	12.6	66.2	26.0	2.5
MDL	44.4	22.8	1.2	1.80	24.3	58.5	37.3	1.6
MDL	80.9	9.4	0.9	0.30	23.6	65.2	32.1	2.0
CLK	25.7	66.4	3.1	1.32	7.1	51.6	26.1	2.0
CLK	61.5	26.0	2.4	0.31	17.2	58.5	29.3	2.0

* EDX surface analysis; carbon free basis

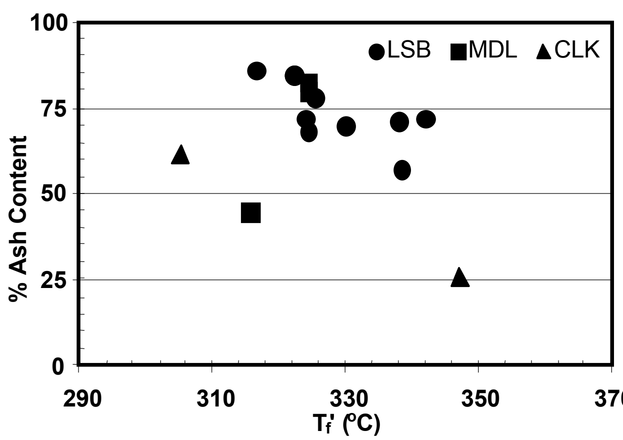

Fig. 10 Plot of wt. % ash content in the deposits vs modified film temperature for all the crudes tested.

Iron and sulphur are commonly reported in crude oil fouling deposits. Lambourn and Durrieu (9) reported iron salts of 20-35 % in deposits from medium crudes, and 75-90% for light (°API >40) crudes. Panchal et al. (10) investigated iron sulphide fouling in gas oils. By adding soluble iron and sulphur as thiophenols at Fe/S ratios of 0.18 to 0.33, his deposits showed Fe/S ratios of 1.8 to 2.2, which are in the range of the current work.

CONCLUSIONS

A study of fouling of three sour Canadian crude oils at bulk liquid temperatures of 250-280°C, and initial surface temperatures in the range 330-380°C has shown:

a) that fouling rates increase strongly with both the surface and the bulk temperature. A 28°C increase in the conventional film temperature causes the fouling rate to double.
b) fouling rate could be correlated using a modified film temperature, which gave more weight to the surface temperature than to the bulk temperature.
c) fouling rate decreased as the velocity was increased to the power -0.35.
d) deposits were rich in mineral matter and in sulphur, indicating the formation of iron sulphide in the deposits.
e) fouling rates at fixed velocity were highest with the heaviest oil, which also contained the most sulphur, and iron.

In all cases, a rise in oil viscosity occurred over the time of re-circulation, which led to an over-estimation of the fouling rate compared to the once-through fouling experiments.

ACRONYMS

BS&W	Bottom sediment and water
CLK	Cold Lake oil
DAS	Data Acquisition System
EDX	Energy Dispersive X-Ray
HTRI	Heat Transfer Research Inc.
LSB	Light Sour Blend oil
MDL	Midale crude oil

NOMENCLATURE

A	area for heat transfer (m^2)
E_f	fouling activation energy (kJ/mol)
I_N	insolubility blending number
P	state of peptization of the crude
Pa	peptizability of asphaltenes
Po	peptizability power of maltenes
Q	heat flow (W)
q	heat flux (kW/m^2)
R	universal gas constant
Re	Reynolds number based on equivalent diameter and film temperature
Re_b	Reynolds number based on equivalent diameter and bulk temperature
R_f	fouling resistance (m^2K/kW)
S_{BN}	solubility blending number

T	temperature (°C)
T_b	average bulk temperature (°C)
T_f'	modified film temperature (°C)
T_f	film temperature (°C)
T_s	surface temperature (°C)
$T_{s,o}$	initial surface temperature (°C)
U	heat transfer coefficient (kW/m^2K)
U_o	clean heat transfer coefficient (kW/m^2K)
V	annular velocity (m/s)
Δ	differential
δ_f	flocculation solubility parameter
δ_{oil}	solubility parameter of the crude

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