

## BLENDING EFFECTS ON FOULING OF FOUR CRUDE OILS

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### ABSTRACT

Blends of various crude oils are often used in refining processes depending on prices and availability. Mixtures of some crude oils in specific proportions have been known to cause significant fouling in refinery preheat trains, usually due to precipitation of asphaltenes. Four crude oils used in Australia (Bach Ho, Gippsland, Cossack and Kutubu) were involved in the study. Compatibility parameters of the oils were determined based on flocculation titrations and SARA analyses. Bach Ho was the heaviest oil and showed the highest fouling rates among the four crude oils. Therefore binary mixtures containing Bach Ho and each of the other three oils were tested for thermal fouling.

The blends were re-circulated in a fouling loop equipped with an annular (HTRI) electrically heated probe, operating at constant heat flux for periods up to 90 hours. Experiments were performed under a nitrogen atmosphere at a pressure of about 379 kPa, bulk temperature of 80°C, velocity of 0.25m/s and initial surface temperature of 240°C. The oil mixtures were tested for filterable solids content, density, and viscosity before and after each fouling run. Fouling rates for the individual oils and the blends are presented and related to various compatibility criteria. Fouling rates of Bach Ho decreased dramatically when blended with substantial levels of the other oils. Data on deposit composition are presented, and the fouling mechanism discussed.

### INTRODUCTION

One of the major costs in petroleum processing is energy loss due to the build up of thermal insulating foulant in pre-heat exchangers. The mitigation of fouling in these units is of interest and was investigated to reduce the cost of lost energy (Polley et al., 2000). Fouling may be caused by asphaltene precipitation, oxidative polymerization and coke formation arising from components in the oil, while salts, sediments and corrosion products arise from impurities (Murphy and Campbell, 1992). Insoluble asphaltenes are considered to be a major cause of fouling in crude oil refining (Dickakian and Seay, 1988). When blending crude oils,

incompatibility and the subsequent precipitation of asphaltenes can cause significant fouling in the preheat train. The oil compatibility model was developed to predict the proportions and order of blending of oils that would avoid incompatibility (Wiehe and Kennedy, 2000).

Asomaning and Watkinson (2000) studied petroleum stability effects on heat exchanger fouling using mixtures of heavy oils containing asphaltenes and carrier fluids consisting of a fuel oil cut with varying amounts of added aliphatics and aromatics. They concluded that at moderate bulk temperature and surface temperatures below 220°C solubility phenomena affect the concentration of asphaltenes in suspension and consequently controls fouling and fouling rate can be roughly correlated to suspended asphaltenes measured by hot filtration, and with the colloidal instability index, CII (Eq. 1):

$$CII = \frac{(\text{Saturates} + \text{Asphaltenes})}{(\text{Aromatics} + \text{Resins})} \quad (1)$$

It is noteworthy that the colloidal instability index alone can not predict fouling over a full range of composition, since for a given sum of the (Resins + Aromatics), one should expect greatly different behavior if either the one or the other of the two terms in the numerator, the saturates or the asphaltenes, went to zero.

Wiehe et al. (2001), found that crude oil fouling in heat exchangers may be caused by nearly incompatible crude oil mixtures in addition to those that are incompatible. The tendency for asphaltenes to adsorb on heated metal surfaces increases as the oil mixture approaches compositions at which asphaltenes precipitate. Their work demonstrated that fouling of heated metal surfaces by asphaltenes does not require the asphaltenes to be insoluble if the blend is nearly incompatible.

Gippsland and Cossack crude oils produced in Australia, Bach Ho from Vietnam and Kutubu from New Guinea, give rise to fouling problems in refineries operated by Caltex Australia, despite their low sulphur, ash and asphaltene levels. In previous papers (Saleh et al., 2004, Saleh et al., 2005) fouling

by the individual oils has been reported. It was shown that fouling was related to the insoluble solids present at low concentrations in these oils. The present work was undertaken to study the effect of mixing and blending the aforementioned crude oils at certain operating conditions, with the intention of using the results to guide a fouling mitigation strategy.

## MATERIALS AND METHODS

Table 1 lists the properties of all crude oils used in this work. Both asphaltene and sulphur contents are low in three of these crudes. The viscosity of Bach Ho at 20°C was more than 10 times higher than values of the other crude oils. This was also reflected by a high pour point of 33°C and an asphaltene concentration over four times that of the other oils. Insoluble solids in the oils, determined by filtration at 85°C through a 3-micron membrane filter, were highest in Bach Ho at 3.86 g/L, and decreased to < 1.5 g/L for Cossack and Kutubu.

Thermal fouling runs were performed using blends of 50 and 75 wt% Bach Ho with the balance of each of the other crudes. The fouling apparatus consists of a re-circulation loop containing a 10-L feed tank and a pump; an orifice plate was used for flow measurement in conjunction with an annular (HTRI) heat transfer probe, which was operated at constant heat flux with time. Each blend was poured into the feed tank, purged with nitrogen and pressurized to 379 kPa. The inlet and outlet bulk temperatures along with the probe surface temperature were measured via thermocouples (Saleh et al, 2005). The fouling resistance was determined at constant heat flux by the decrease in heat transfer coefficient with time for periods of 30 – 90 hours.

An automated flocculation titrimeter (AFT) apparatus developed by Western Research Institute, and described by Pauli (1996), was used in an attempt to measure the onset-point (flocculation point) of all crude oils using iso-octane as titrant, toluene as solvent and heavy oil as reference. The AFT consists of intersecting sample circulation and titration loops.

Four samples of crude oil ( $V_o$ ) are transferred to reaction vials, and different amounts of toluene ( $V_s$ ), added to dissolve the asphaltene. Thus, each vial contains a solution of a different concentration of asphaltene in toluene. Each of the solutions is titrated with precipitant ( $V_p$ ) iso-octane or heptane at a constant titrant delivery rate. The flocculation points were determined from the transmittance at 740 nm.

To predict the stability of the oil blends compatibility models of Andersen and Pedersen, and of Wiehe were applied. The solubility parameter values for toluene and n-heptane were taken from literature (Z.Yang et al, 1999) where  $\delta_T = 18.3 \text{ MPa}^{0.5}$  and  $\delta_H = 15.2 \text{ MPa}^{0.5}$ .

From the plots of the  $V_p/V_o$  versus  $V_s/V_o$ , the model of Andersen and Pedersen (1999) is used to determine the critical solubility parameter  $\delta_{cr}$  (Eq. 2), and  $\delta_o$ . The  $\delta_{cr}$  can be calculated from the following equation:

$$\delta_{cr} = \phi_o \delta_o + \phi_H \delta_H + \phi_T \delta_T \quad \text{and} \quad \sum \phi_i = 1 \quad (2)$$

The oil is stable if  $\delta_o > \delta_{cr}$ . Similarly, a stability criterion can be written for the Wiehe model. The flocculation solubility parameter,  $\delta_f$ , found from titrations of the oil is given as:

$$\delta_f = \phi_T \delta_T + \phi_H \delta_H + \phi_o \delta_o \quad (3)$$

For stability, the insolubility number,  $I_N$ , which measures degree of insolubility of the asphaltene present in the oil, must be less than the solubility blending number,  $S_{BN}$ , which measures the solvency of the oil for asphaltene.

$$I_N = 100 \frac{(\delta_f - \delta_H)}{(\delta_T - \delta_H)} \quad (4)$$

$$S_{BN} = 100 \frac{(\delta_{oil} - \delta_H)}{(\delta_T - \delta_H)} \quad (5)$$

In order for mixtures of oils to be compatible, the solubility blending number of the mixture should be higher than the maximum insolubility number of any of the individual oils in the mixture.

**Table 1.** Properties of crude oils used in this study.

| Properties                   | Bach Ho | Gippsland | Cossack | Kutubu |
|------------------------------|---------|-----------|---------|--------|
| Density (g/ml) at 20 °C      | 0.82    | 0.79      | 0.79    | 0.80   |
| API Gravity                  | 40.80   | 47.10     | 47.30   | 44.40  |
| Vapor Pressure (37 °C) psi   | 3.00    | 6.00      | 7.00    | 9.00   |
| Total Sulfur (wt%)           | 0.03    | 0.12      | 0.12    | 0.03   |
| Total Nitrogen (PPM)         | 398     | 120       | 310     | -      |
| Viscosity (mPa.s) at 20 °C   | 22.2    | 1.96      | 1.84    | 2.01   |
| Ash (wt%)                    | -       | <0.01     | <0.01   | -      |
| Asphaltenes (wt%)            | 1.48    | 0.35      | 0.08    | 0.11   |
| Pour point (°C)              | 33      | -42       | -18     | 3      |
| Insolubles ( T = 85°C) (g/L) | 3.86    | 1.95      | 1.46    | 1.30   |

The solubility blending number of a mixture of oils is the volumetric average for those oils, calculated as follows:

$$S_{BNmix} = \frac{V_1 S_{BN1} + V_2 S_{BN2} + V_3 S_{BN3} + \dots}{V_1 + V_2 + V_3 + \dots} \quad (6)$$

Hence, the compatibility criterion for oil mixtures can be defined as follows,

$$S_{BNmix} > I_{Nmax} \quad (7)$$

## RESULTS AND DISCUSSION

### Compatibility Tests:

Saturates, aromatics, resins and asphaltene (SARA) analysis was conducted at the National Centre for Upgrading and Technology (NCUT), Canada, on the crude samples using ASTM D-2007. Results are presented in Table 2.

**Table 2.** Combined analysis (SARA+PIONA) (ASTM D-2007) and colloidal instability index for all oils.

|             | Bach Ho (wt%) | Gippsland (wt%) | Cossack (wt%) | Kutubu (wt%) |
|-------------|---------------|-----------------|---------------|--------------|
| Saturates   | 89.01         | 81.60           | 77.68         | 79.51        |
| Aromatics   | 6.54          | 15.66           | 19.43         | 16.97        |
| Polars      | 2.98          | 2.39            | 2.82          | 3.40         |
| Asphaltenes | 1.48          | 0.35            | 0.08          | 0.11         |
| CII         | 9.51          | 4.54            | 3.50          | 3.91         |

Oils with CII > 1 tend to be unstable, and precipitate asphaltenes. Hence all oils are unstable according to this criterion, however asphaltene concentrations are low in three of the oils.. Since Bach Ho has the largest amount of asphaltenes present, it would be expected to be the most likely to give rise to measurable rates of asphaltene deposition.

**Table 4.** Calculated compositions of test mixtures

| Test Fluid               | Calculated Saturates Content (%) | Calculated Aromatics Content (%) | Calculated Polars Content (%) | Calculated Asphaltenes Content (%) | CII  | $\delta_o$ (M Pa) <sup>0.5</sup> | $S_{BN,mix}$ |
|--------------------------|----------------------------------|----------------------------------|-------------------------------|------------------------------------|------|----------------------------------|--------------|
| 75%Bach Ho-25% Gippsland | 87.16                            | 8.82                             | 2.83                          | 1.20                               | 7.58 | 16.19                            | 33.14        |
| 50%Bach Ho-50% Gippsland | 85.31                            | 11.10                            | 2.69                          | 0.92                               | 6.25 | 16.26                            | 35.93        |
| 75%Bach Ho-25% Cossack   | 86.18                            | 9.76                             | 2.94                          | 1.13                               | 7.18 | 16.25                            | 36.12        |
| 50%Bach Ho-50% Cossack   | 83.35                            | 12.99                            | 2.90                          | 0.78                               | 5.69 | 16.39                            | 40.28        |
| 75%Bach Ho-25% Kutubu    | 86.64                            | 9.15                             | 3.09                          | 1.14                               | 6.87 | 16.61                            | 47.94        |
| 50%Bach Ho-50% Kutubu    | 84.26                            | 11.76                            | 3.19                          | 0.80                               | 5.30 | 17.10                            | 63.92        |

Initially the flocculation titration experiments were conducted using Bach Ho by itself at sample weights of 0.5, 0.75, 1, 2, 3 and 4 g with 3 or 0.5 ml of toluene. The oil-toluene mixtures did not flocculate detectable quantities of asphaltenes on their own possibly due to the low asphaltene concentration in the samples; hence Heavy Oil was used as a reference in all tests. This meant that the flocculation point of the oils themselves could not be measured, but the solvent properties of the oils for asphaltenes could be determined. Results are presented in Table 3.

**Table 3.** Solubility parameters for all crude oils using heavy oil \* as a reference.

| Oil Type                        | Heavy Oil | Bach Ho | Gippsland | Cossack | Kutubu |
|---------------------------------|-----------|---------|-----------|---------|--------|
| $\delta_o$ (MPa) <sup>0.5</sup> | 19.04     | 16.12   | 16.39     | 16.65   | 18.07  |
| $S_{BN}$                        | 128       | 30.82   | 39.91     | 48.61   | 95.89  |

\*  $\delta_{cr}$  or  $\delta_r$  (MPa)<sup>0</sup> = 16.21;  $I_N$  = 33.84

The insolubility number for asphaltenes based on heavy oil is 33.84. Bach Ho, with  $S_{BN}$  30.82, is the only oil with  $S_{BN}$  < 33.84. Gippsland, Cossack and Kutubu have increasing solubility blending numbers of 39.93, 48.61 and 95.89 respectively. Once the insolubility and the solubility blending numbers of a set of crude oils have been measured, potentially incompatible pairs of oils can be predicted and compared by experimentally blending a number of crudes in different proportions. The criterion for compatibility of any blend is given by Equation 7. Calculated oil constituent contents of test blends along with their CII values are presented in Table 4.

Except for the first mixture of 75% Bach Ho-25 % Gippsland, which has an  $S_{BN}$  of 33.1, all mixtures have  $S_{BN}$  values which would exceed the insolubility number of  $I_N = 33.8$  for asphaltenes. Hence all other mixtures should be compatible.

### Blending Experiments:

Fouling tests were performed on three sets of crude oil blends. All tests were conducted at initial surface temperature of  $240 \pm 5^\circ\text{C}$ , average bulk temperature of  $81 \pm 4^\circ\text{C}$  and a velocity of 0.25 m/s. These conditions were chosen based on previous experiments conducted on each of these oils where maximum fouling was observed (Saleh et al., 2004, 2005).

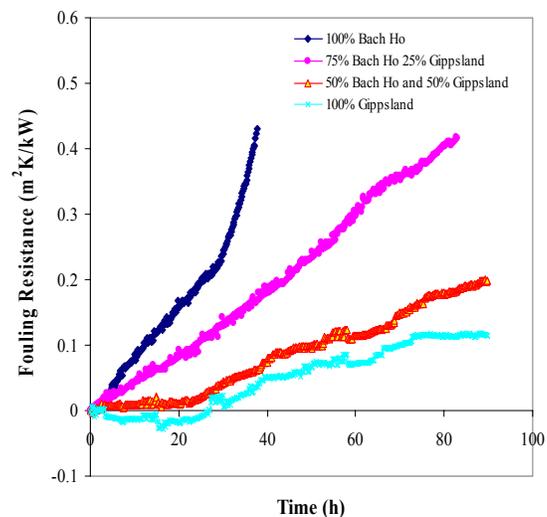
Results of fouling experiments, and final insolubles contents in the oils are presented in Table 5. The curve of fouling resistance versus time for 100% Bach Ho (Figure 1) has two segments. For this oil both the rate for the first segment and the average for both segments are reported. The procedure for determining the initial rate is given in Saleh et al., 2005.

### Bach Ho – Gippsland Blends

Bach Ho-Gippsland blends were investigated first because they have the lowest solubility blending numbers (Table 3). Fouling tests were carried out using blends of 75wt.% Bach Ho – 25wt.% Gippsland and 50wt.% Bach Ho – 50wt.% Gippsland. Data are compared in Figure 1 with results from previous fouling tests conducted using 100wt.% Bach Ho and 100wt.% Gippsland. For the 100wt.% Bach Ho run, fouling resistance increases linearly over the first ~ 30-h to ~  $0.23 \text{ m}^2\text{K/kW}$ , after which fouling resistance appeared to accelerate to  $0.43 \text{ m}^2\text{K/kW}$  at 38-h. Using 25wt.% Gippsland, after 30-h the fouling resistance was  $0.13 \text{ m}^2\text{K/kW}$  (i.e. 56% of the value for Bach Ho alone). Increasing the content of Gippsland in the blend to 50wt.%, the

fouling resistance at  $t = 30 \text{ h}$  decreased to  $0.04 \text{ m}^2\text{K/kW}$ , a value 17 % of that for the Bach Ho alone.

Fouling rates decreased with increasing Gippsland fraction in the blend (Figure 2) due to the decrease in amount of filterable insolubles, asphaltenes, and saturates and compared to 100 wt.% Bach Ho. The drop in fouling rate at 50 % Gippsland is greater than expected if rates were linearly dependent on percentage Gippsland in the blend.



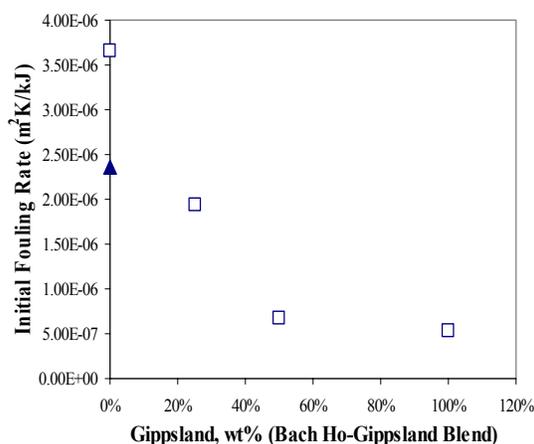
**Figure 1.** Fouling resistance vs. time for Bach Ho-Gippsland blends.

**Table 5.** Fouling results for crude oils and their blends.

| Crude Blend              | Re.  | $U_0$<br>(kW/m <sup>2</sup> K) | $U_0$ , final<br>(kW/m <sup>2</sup> K) | $R_f$ , final<br>(m <sup>2</sup> K/kW) | $(dR_f/dt)_0$<br>(m <sup>2</sup> K/kJ) | *Initial<br>Filterable<br>Insolubles<br>(g) | Final<br>Filterable<br>Insolubles<br>(g) |
|--------------------------|------|--------------------------------|--|--|--|---|--|
| 100%Bach Ho **           | 1584 | 2.23                           | 1.16                                   | 0.43                                   | 3.65E-06                               | 38.62                                       | 18.86                                    |
| 75%Bach Ho-25% Gippsland | 1700 | 2.32                           | 1.18                                   | 0.42                                   | 1.94E-06                               | 33.20                                       | 20                                       |
| 50%Bach Ho-50% Gippsland | 1828 | 2.40                           | 1.63                                   | 0.20                                   | 6.66E-07                               | 28.40                                       | 22.45                                    |
| 100%Gippsland            | 2071 | 2.18                           | 1.74                                   | 0.12                                   | 5.08E-07                               | 18.88                                       | 16.8                                     |
| 75%Bach Ho-25% Cossack   | 1740 | 2.46                           | 1.47                                   | 0.27                                   | 8.61E-07                               | 31.60                                       | 22.4                                     |
| 50%Bach Ho-50% Cossack   | 1867 | 2.48                           | 1.94                                   | 0.11                                   | 3.88E-07                               | 26.24                                       | 22.7                                     |
| 100%Cossack              | 2150 | 2.61                           | 2.36                                   | 0.04                                   | 1.49E-07                               | 14.61                                       | 13.11                                    |
| 75%Bach Ho-25% Kutubu    | 1780 | 2.38                           | 1.47                                   | 0.26                                   | 8.33E-07                               | 31.20                                       | 22.6                                     |
| 50%Bach Ho-50% Kutubu    | 1892 | 2.21                           | 1.77                                   | 0.11                                   | 3.61E-07                               | 25.20                                       | 22.5                                     |
| 100%Kutubu               | 2200 | 2.35                           | 2.19                                   | 0.03                                   | 1.16E-07                               | 12.96                                       | 11.6                                     |

\* in 10-L oil

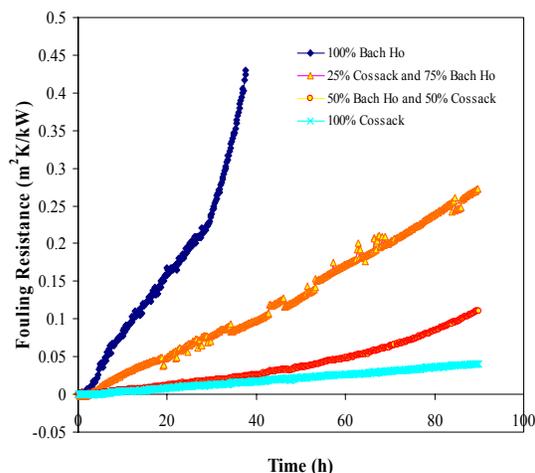
\*\* Fouling Rate  $2.3\text{E}-06 \text{ m}^2\text{K/kJ}$  over first 30 hours.



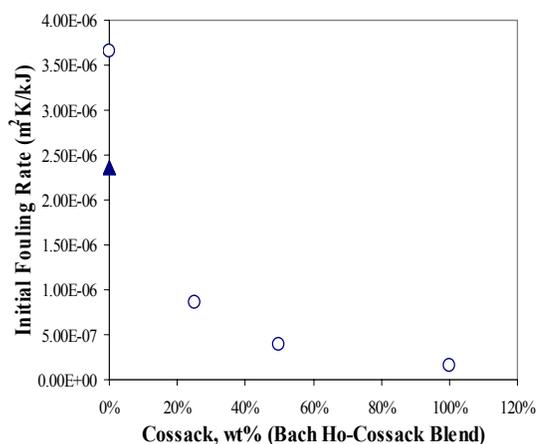
**Figure 2.** Fouling rates vs. percentage of Gippsland in Bach Ho-Gippsland blends.

**Bach Ho – Cossack Blends**

As with Gippsland, fouling tests were performed using blends of 75wt% Bach Ho and 50 % Bach Ho in Cossack. Data were compared (Figure 3) with results from previous tests conducted using 100wt% Bach Ho and 100wt% Cossack. At t=30-h, the fouling resistance decreased from 0.23 m<sup>2</sup>K/kW with 100% Bach Ho by some 66% and 95 % respectively as the % Cossack in the blend was raised from 25% to 50%. For the higher concentration of Cossack oil, fouling at the 90-h duration was exceedingly small. This drastic reduction in extent of fouling is reflected in Figure 4 where the rates are plotted versus composition. As indicated in Table 5, the rate at 50 % Cossack was about 10 % of that for pure Bach Ho.



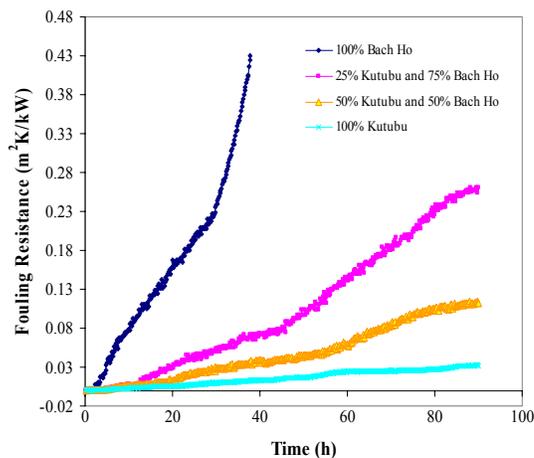
**Figure 3.** Fouling resistance vs. time for Bach Ho-Cossack blends.



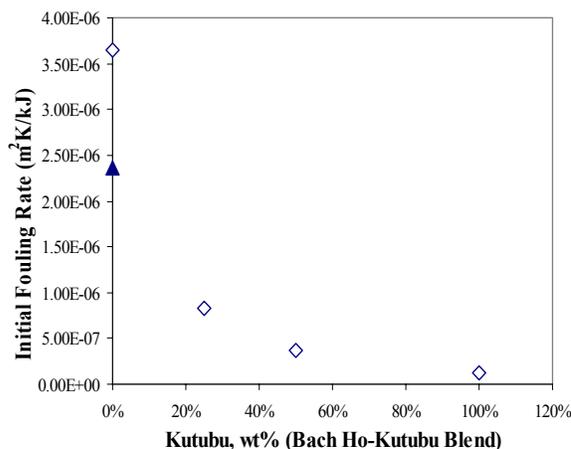
**Figure 4.** Fouling rates vs. percentage of Cossack in Bach Ho-Cossack blends.

**Bach Ho – Kutubu Blends**

Bach Ho was also blended with Kutubu at 75wt% Bach Ho – 25wt% Kutubu and 50 wt% Bach Ho – 50% Kutubu. Data were compared with results from previous tests conducted using 100wt% Bach Ho and 100wt% Kutubu. As with Cossack oil, blending 25 % and 50 % of Kutubu with Bach Ho, reduced fouling resistance at 30-h from 0.23 to 0.05 and 0.03 m<sup>2</sup>K/kW respectively, as shown in Figure 5. The decreases in fouling rates, given in Table 5 and plotted in Figure 6 are also very substantial. With 50 % Kutubu, the fouling rate is about 1/10 that of the pure Bach Ho.



**Figure 5.** Fouling resistance vs. time for Bach Ho-Kutubu blends.



**Figure 6.** Fouling rates vs. percentage of Kutubu in Bach Ho-Kutubu blends.

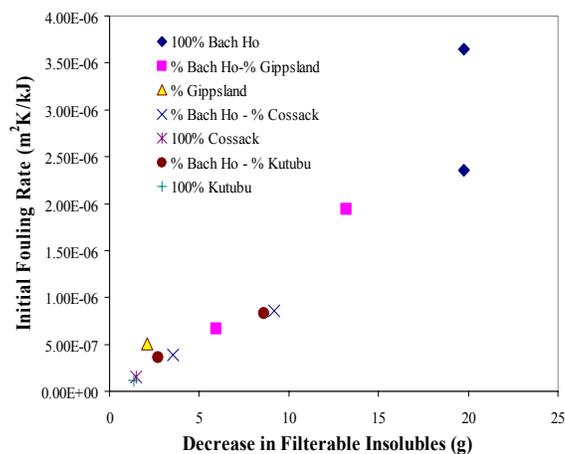
### FOULING RATES & STABILITY OF BLENDS

Three parameters related to stability of the blends were used to correlate the fouling rates: concentration of filterable insolubles, colloidal instability index, and solubility blending number.

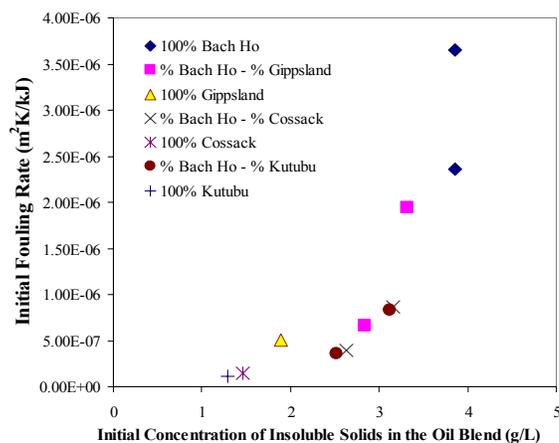
#### Filterable Insolubles

Prior work with these individual oils (Saleh et al., 2004, 2005) had identified the presence of particulates as the primary cause of fouling. It is also evident from Table 5 that blends with the highest insoluble solids contents showed the highest fouling rates, and those with the lowest insoluble solids contents showed the lowest fouling rates. The concentration of insoluble suspended particles decreased over each run, as has been noted previously. If the fouling rate is constant with time, it should be related to the decrease in mass of suspended particles. In Figure 7, the fouling rate is plotted versus the decrease in amount of suspended solids from the beginning to the end of each experiment. In all cases the increases in fouling rate paralleled the decreases in the amount of filterable insolubles. The linearity of this plot tends to confirm the observation that fouling is related to the insoluble solids present in the oil blends

Figure 8 shows the fouling rate plotted versus the initial concentration of insoluble solids in the oil blend. These initial concentrations values were based on simple mixing calculations of solids content of the pure oils. At concentrations below about 2.5 g/L, fouling rate depends linearly upon concentration, however overall the plot is highly non-linear.



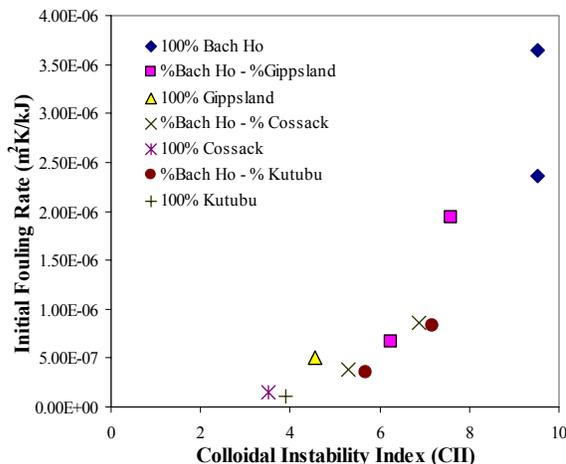
**Figure 7.** Initial fouling rate versus the decrease in filterable insolubles over the run duration.



**Figure 8.** Initial fouling rate versus the initial concentration of insoluble solids in the oil blend.

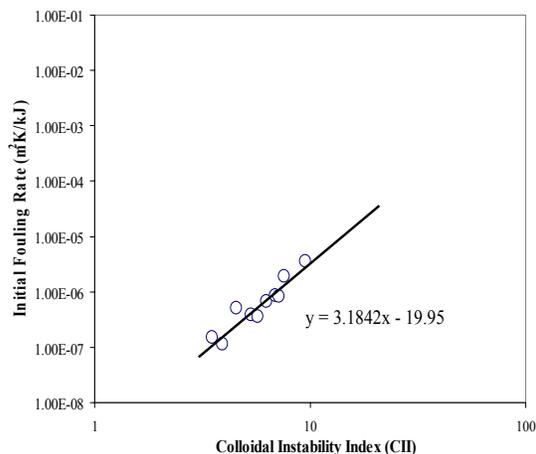
#### Colloidal Instability Index

The initial fouling rate also was found to correlate well with the colloidal instability index for the oils and the blends (Figure 9), where within the scatter of the results; all data appeared to collapse to a single curve. This curve is similar to that of Figure 8, because the initial solids concentration of each oil correlated with its colloidal instability index (Tables 1 and 2). Fouling rates of heavy oil-diluent blends containing concentrations of asphaltenes up to 3.2 % have been shown previously (Asomaning and Watkinson, 2000) to increase strongly with both CII and suspended asphaltenes content.



**Figure 9.** Initial fouling rate vs. colloidal instability index (CII).

A log-log plot of initial fouling rate versus colloidal instability index (CII) yielded a straight line (Figure 10), corresponding to the following equation:



**Figure 10.** Log-log plot of initial fouling rate vs. colloidal instability index (CII).

$$\frac{dR_f}{dt} = a(CII)^n \tag{8}$$

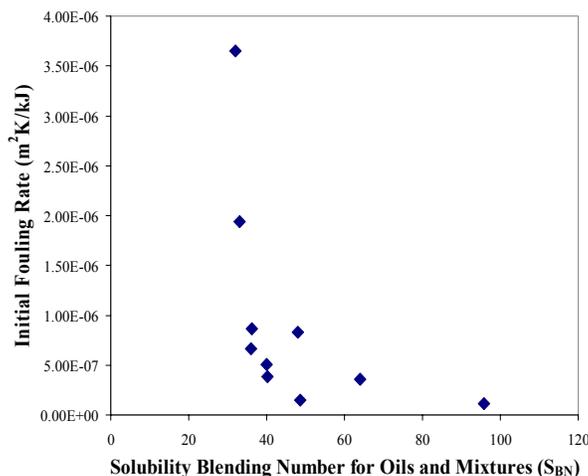
where the constant  $a = 2.17E-09 \text{ m}^2\text{K/kJ}$ , and the exponent on the colloidal instability index (CII),  $n = 3.2$ . The parameter “a”, is the fouling rate at  $CII = 1$ , i.e.

$$\frac{dR_f}{dt} = \left. \frac{dR_f}{dt} \right|_{CII=1.0} \cdot (CII)^n \tag{9}$$

At a colloidal instability index,  $CII = 1$ , the rate is  $0.0217E-07 \text{ m}^2\text{K/kJ}$ , which is about 3 % of the smallest fouling rate measured in this work. This supports the postulate that fouling rate approaches zero for  $CII = 1$ .

**Solubility Blending Number of Oils and Mixtures**

A plot of fouling rate versus solubility blending number of oils and mixtures did not collapse the data onto a single curve as was found with CII in Figure 9. This behaviour is apparent in Figure 11, where the data appears to show two separate branches at  $S_{BN}$  greater than about 35.



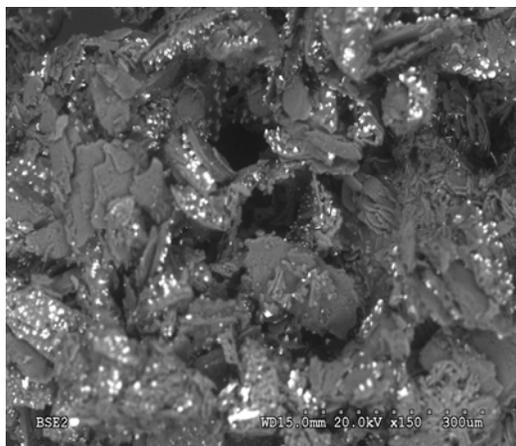
**Figure 11.** Initial fouling rate vs. solubility blending number for oils and mixtures.

Correlations of fouling rate with solubility blending number and initial insoluble solids concentration showed more scatter than with CII. Hence the CII appeared to be the preferable parameter to relate to fouling rates for these blends.

**DEPOSIT ANALYSIS**

The deposit that built up on the heated section as the run proceeded appeared as a thin black layer of carbonaceous material on the surface. At the end of each run, after rinsing the probe with varsol and then acetone, the deposit was collected using a brush or a metal blade, depending on how strongly it was packed or adhered to the probe.

Micrographs from the scanning electron microscope (SEM) show clusters of agglomerations of asphaltene-like structures that have undergone some form of chemical change on the hot probe surface (Figure 12).



**Figure 12.** Probe deposit morphology under SEM for 50wt%Bach Ho – 50wt% Gippsland.

An EDX analyzer attached to the SEM is used to examine the deposit for the presence of elements at the surface using carbon as the standard. The presented results are average of three points at the surface of deposits. The EDX analysis (Table 6) shows the presence of C, O, S, and in some cases traces of iron in the surface structure of the deposits. EDX does not report hydrogen content. Copper, which apparently originated from a brass shaft cover in the pump, was also detected in all deposits. Other metals such as calcium and magnesium were below detection levels.

**Table 6.** Surface analysis for deposits by EDX.

| Crude Blend              | C (wt%) | O (wt%) | S (wt%) | Fe (wt%) |
|--------------------------|---------|---------|---------|----------|
| 100% Bach Ho             | 85.85   | 12.14   | 1.06    | 0.15     |
| 75%Bach Ho-25% Gippsland | 85.65   | 8.07    | 2.41    | -        |
| 50%Bach Ho-50% Gippsland | 86.23   | 7.78    | 3.04    | -        |
| 75%Bach Ho-25% Cossack   | 89.70   | 5.22    | 1.58    | 0.46     |
| 50%Bach Ho-50% Cossack   | 78.20   | 8.79    | 3.60    | 0.68     |
| 75%Bach Ho-25% Kutubu    | 89.53   | 5.90    | 1.82    | 0.89     |
| 50%Bach Ho-50% Kutubu    | 87.39   | 6.04    | 2.73    | -        |
| 100 %Bach Ho*            | 87.94   | 10.44   | 0.08    | -        |
| 100% Gippsland*          | 72.16   | 21.33   | 1.06    | 0.43     |

\* Filtered solids

Oxygen content averaged 7.7 wt.% in the surface of the deposits. This oxygen can be in both organic and inorganic forms. Sulphur averaged 2.3 wt.% in the deposit EDX analyses. Iron ranged from undetectable to 0.9 wt.%.

Thermogravimetry was used to determine bulk deposit ash content. Ash levels, which were below 5 % wt. in all deposits, were highest for 75%Bach Ho-25%Gippsland blend at 4.23 wt.% and lowest for 50%Bach Ho-50%Kutubu at 2.12 wt.%. Ash content in deposits increased with increasing the fraction of Bach Ho in the blends with all three other oils.

Bulk chemical analysis of collected deposits is shown in Table 7. For all deposits, average values in % wt. were as follows: carbon 78.1 %, hydrogen 7.24%, sulphur 3.46 %, nitrogen 1.6 %, and ash 3.4 %. Oxygen, which is estimated by difference, and hence incorporates errors of the other analyses averaged 6.3 wt %. Thus average atomic ratios for the deposits are H/C = 1.11, and S/C = 0.017. The H/C ratio is within the range of  $1.15 \pm 0.05$  for asphaltenes given by Speight (1991), whereas the S/C ratio of 0.017 is slightly lower than the expected range of  $0.03 \pm 0.005$ . Thus the deposits appear to contain asphaltene-like species, degraded somewhat after several days on the heated surface. Tests showed deposits to be only partially soluble in toluene, and hence were not pure asphaltenes.

Analyses of solids filtered from Gippsland and Bach Ho oils are also given in Tables 6 and 7. The bulk sulphur content of the suspended solids (0.5-0.6 %) is markedly lower than that of the average deposit (3.5%), and the ash is lower by a factor of 3-4. Therefore, both sulphur and ash are concentrated in the deposits to levels above those in the particulates. Further work is needed to relate suspended solids and deposit compositions.

**Table 7.** Chemical analysis of collected deposits.

| Composition             | C     | O**  | S    | N    | H    | Ash  | H/C  |
|-------------------------|-------|------|------|------|------|------|------|
| 100% Bach Ho            | 80.58 | 2.82 | 2.66 | 1.44 | 7.60 | 4.90 | 1.13 |
| 100%Gippsland           | 76.50 | 9.88 | 2.99 | <0.3 | 7.80 | 2.53 | 1.22 |
| 50%Bach Ho-50%Gippsland | 77.33 | 7.68 | 3.35 | 1.28 | 6.85 | 3.51 | 1.06 |
| 75%Bach Ho-25%Gippsland | 80.27 | 4.58 | 2.31 | 1.67 | 6.94 | 4.23 | 1.03 |
| 100%Cossack             | 81.76 | 2.42 | 3.93 | 1.67 | 8.21 | 2.01 | 1.20 |
| 50%Bach Ho-50%Cossack   | 76.29 | 5.41 | 6.26 | 2.08 | 7.26 | 2.70 | 1.14 |
| 75%Bach Ho-25%Cossack   | 73.75 | 9.53 | 4.32 | 1.31 | 7.67 | 3.42 | 1.25 |
| 100%Kutubu              | 82.27 | 3.44 | 3.42 | 1.58 | 7.74 | 1.55 | 1.13 |
| 50%Bach Ho-50%Kutubu    | 78.70 | 6.4  | 3.22 | 2.33 | 7.23 | 2.12 | 1.10 |
| 75%Bach Ho-25%Kutubu    | 79.58 | 7.44 | 2.12 | 0.81 | 7.12 | 2.93 | 1.07 |
| 100 %Bach Ho*           | 86.81 | 2.44 | 0.6  | 1.08 | 7.22 | 1.85 | 1.06 |
| 100%Gippsland*          | 88.3  | 0.35 | 0.5  | 0.90 | 9.20 | 0.75 | 1.25 |

\* Filtered solids \*\* By difference

## CONCLUSIONS

A study of fouling of Bach Ho crude oil in binary blends with, Gippsland, Cossack and Kutubu crude oils led to the following conclusions:

- Fouling rates of individual oils decreased with decreasing asphaltene and suspended solids content, decreased colloidal instability index and increasing solubility blending number. The importance of particulate fouling was proven by significant decreases in the amount of suspended solids over each run. The fouling rate was linearly related to the magnitude of this decrease.
- Blending Bach Ho oil with oils of higher solubility blending number or lower colloidal instability index, filterable solids, and asphaltene content resulted in a significant decrease in extent of fouling at a given time, and in fouling rate.
- The effect of blending on fouling rate appeared to be non-linear, and moderate percentages of blending oil resulted in relatively larger decreases in fouling rate.
- For oils and their mixtures, the initial fouling rate could be correlated with the colloidal instability index (CII) or with more scatter, to the concentration of insoluble solids.
- Deposits contained hydrocarbons with H/C atomic ratio of 1.11, about 3.5 % sulphur and less than 5 wt % ash.

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## NOMENCLATURE

|           |  |
|-----------|--|
| CII       | colloidal instability index  |
| HTRI      | Heat Transfer Research Institute   |
| $I_N$     | insolubility number  |
| PFRU      | portable fouling research unit   |
| Re        | Reynolds number based on equivalent diameter and average bulk properties |
| $R_f$     | fouling resistance, $m^2K/kW$  |
| SARA      | Saturates, Aromatics, Resins and Asphaltenes                             |
| $S_{BN}$  | solubility blending number   |
| SEM       | Scanning Electron Microscope   |
| t         | time, h  |
| $T_b$     | bulk temperature, °C   |
| $T_{s,o}$ | initial surface temperature, °C  |
| u         | fluid velocity, m/s  |
| U         | overall heat transfer coefficient $kW/m^2K$                              |
| $U_o$     | clean heat transfer coefficient $kW/m^2K$                                |

|          |                                     |
|----------|-------------------------------------|
| V        | volume, L                           |
| $\mu$    | dynamic viscosity, Pa.s             |
| $\delta$ | solubility parameter, $(MPa)^{0.5}$ |
| $\phi$   | volume fraction of solvents and oil |
| $\rho$   | density, $kg/m^3$                   |

Subscripts:

|     |              |
|-----|--------------|
| cr  | critical     |
| f   | flocculation |
| H   | heptane      |
| mix | mixture      |
| o   | oil          |
| p   | precipitant  |
| s   | solvent      |
| T   | toluene      |

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