CRUDE OIL FOULING: PETRONAS REFINERIES EXPERIENCE

M.S. Rafeen\textsuperscript{1}, M.F. Mohamed\textsuperscript{2}, M.Z. Mamot\textsuperscript{3}, N.A. Manan\textsuperscript{4}, Dr A. Shafawi\textsuperscript{5}, Dr M. Ramasamy\textsuperscript{6}

\textsuperscript{1-5}PETRONAS Group Research, Lot 3288 & 3289, Off Jln Ayer Itam, Kawasan Institusi Bangi, 43000 Kajang, Selangor, Malaysia.
\textsuperscript{6}Department of Chemical Engineering, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 31750 Tronoh, Perak, Malaysia.

ABSTRACT
Managing crude oil fouling has been a challenge in PETRONAS refineries. Over the past several years, numerous initiatives have been conducted in order to have better control of the situation \cite{1}\cite{2}\cite{3}\cite{4}. The control strategy currently implemented is to periodically clean the heat exchanger based on the heat exchanger monitoring parameter and supported by antifouling chemical injection program. A review was conducted in one of PETRONAS' refineries in order to come up with a better fouling control strategy. The review is separated into two parts.

Firstly, the plant operational data for two selected hot pre-heat exchanger trains was analyzed. From the analysis, deposition build-up is apparent for only one exchanger train despite both trains receiving the same crude blend. It seems that there are several significant parameters which caused one of the exchanger to fall into fouling threshold region. EXPRESS \cite{5} software was used to evaluate the fouling threshold region for the heat exchanger.

Secondly, foulant sample obtained from the heat exchangers were subjected to analytical testing to investigate the constituent of the foulant. The analyses show that it is mainly organic in nature with a minor portion of the inorganic content made up of mostly corrosion products, salt and sand.

INTRODUCTION
Managing crude oil fouling has been a challenge in PETRONAS refineries and numerous initiatives have been undertaken for the past years in order to have better control \cite{1}\cite{2}\cite{3}\cite{4}. Studies performed found out that high temperature profile, velocity profile and incompatibility of the crude mixing has become the major factor for the crude oil fouling in the hot preheat train network\cite{1}\cite{2}\cite{3}\cite{4}.

Recent studies indicate that crude mixing can cause aggregation and precipitation of asphaltene due to the chemical reaction between paraffinic constituents and stabilizing resins of asphaltene micelle \cite{5}.

The current global market trend for the crude shows that the crude trend has changed to heavier and more acidic crude \cite{6}. The ability to process this type of crude by utilizing the current refinery setup and configuration is an advantage to the refiners. Hence, the capability in tackling crude oil fouling problem need to be enhanced due to the nature of crude which is more prone to fouling.

In one of PETRONAS refineries, fouling factor values are closely monitored and optimum cleaning time was decided to minimize the effect of fouling. In addition to that, an antifoulant program was done to complement the cleaning exercise. There is a need to review and improve the current control and mitigation strategy to achieve better plant operational and economic performance.

PETRONAS has taken the opportunity to perform a fouling baseline study in order to come up with better control and mitigation strategies. The objectives of the study are:

- To study and determine the fouling behavior and threshold region for two hot preheat exchanger (A & B)
- To identify the types of impurities in the foulant samples collected from two hot preheat exchanger (A & B)

For a baseline study, three type of analysis that needs to be done are:

- Past operating data analysis
- Analytical testing
- Experimental analysis

In this phase of the study, two of the above analyses were performed to have an overview of the fouling issue in the refinery.

PAST OPERATING DATA ANALYSIS
Prior to past operating data analysis, several important data were collected from the refinery. The data were obtained from a few sources: Plant Info system, equipment datasheet and inspection history data.

The data collected from the refinery are:

- Past operating data for the past three years (Jan '04 – Jan '07) from Plant Info system: pressure, temperature, flowrate, heat transfer coefficient, duty
- Crude assay library
• Crude plan rates for the past three years (Jan '04 – Jan '07)
• Fouling factor values calculated using simulation tool (Jan '06 – Mar '07)
• Fouulant analysis report
• Visual observation for exchanger A & B
• Test run report
• Datasheet for exchanger A & B

Based on the collected data, two type of analysis were performed to study the fouling behavior and threshold region for the selected exchanger A & B. Data trending analysis and fouling threshold analysis were done for the past operating data.

For data trending analysis, selected past operational data were plotted to see the fouling behavior of the heat exchanger for the past three years. The data selected for the data trending analysis are:

• Heat transfer coefficient
• Duty
• Temperature difference across tube
• Pressure difference across tube
• Flowrate for shell and tube side

In addition to the data trending analysis, a fouling threshold region analysis was performed to determine the performance of the selected exchanger with regard to the current configuration and operating envelope. The fouling threshold analysis was conducted using the EXPRESS software where it utilized Ebert-Panchal model [5] for fouling prediction.

ANALYTICAL TESTING
With regard to the foulant samples, it was taken after the heat exchanger was purged using steam. Then, appropriate analytical testing was conducted to determine the source of foulant constituent. The analytical testing was divided into inorganic and organic compositional analysis.

Apart from that, visual observation was also conducted for both exchanger A & B.

Visual Observation
This exercise shall show the nature of fouling occurred on tube surface morphology using digital camera at normal magnification.

Inorganic Analysis of Foulant
Loss on ignition (LOI) analysis method is used to estimate organic matter and inorganic content in foulant samples. The inorganic parts from LOI are analysed using Scanning Electron Microscope Energy Dispersive X-Ray (SEM-EDAX) for elemental and X-Ray Diffraction (XRD) for compound analysis.

Organic Analysis of Foulant
The distribution of carbon will be shown by High Temperature Gas Chromatography (HTGC) up to Carbon 50. The asphaltene content (in wt %) analysis follows IP 143 /90 (ASTM D 3279-90) [7] test method.

RESULTS
Trending for heat exchanger A & B was performed using the identified operational data. In order to have more accurate information, data reconciliation was done to remove any insignificant and high-variation data. This is important because the data will be used for the development, evaluation and characterization of models for prediction of crude fouling.

Figure 1 and Figure 2 below shows the result of the data trending.

![Figure 1. Data Trending for Selected Operational Data for Heat Exchanger A](http://dc.engconfintl.org/heatexchanger2007/4)
Further analysis on the past operating data was done to determine the fouling threshold region for the selected heat exchanger. Plant monitoring data (e.g. fouling factor) was used as the input values into the EXPRESS software. This will then be used as the basis for the fouling prediction using Ebert-Panchal model [5].

Figure 3 and Figure 4 below are the graphical representation of the EXPRESS software results for heat exchanger A.

Figure 3. Crude Oil Fouling Rates for Measured Data and Predicted Model for Heat Exchanger A

Figure 4. Fouling Threshold Model for Heat Exchanger A

Figure 5 and Figure 6 shows the visual condition of heat exchanger A & B’s tube sheet respectively.

Figure 5. Visual Observation for Heat Exchanger A

Figure 6. Visual Observation for Heat Exchanger B
The test shows that heat exchanger A has a foulant layer build up on the tube sheet and tube internal with some white crystal deposit. However, heat exchanger B turns out to be clean with very minimal fouling.

The foulant samples obtained from the heat exchangers were subjected to several analytical testing to investigate its constituent. The results are as explained in the following paragraph.

LOI analysis result show that the foulant sample is organic in nature. High organic content in the sample is expected as the heat exchangers under study are post desalter unit. Table 1 shows the results of LOI analysis conducted for the foulant samples.

<table>
<thead>
<tr>
<th></th>
<th>Organic (wt%)</th>
<th>Inorganic (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>81</td>
<td>19</td>
</tr>
<tr>
<td>B</td>
<td>89</td>
<td>11</td>
</tr>
</tbody>
</table>

For XRD analysis, the result of the analysis indicates that the inorganic compounds in the foulant sample are mostly corrosion products (FeS₂, Fe₃O₄), salt (CaSO₄) and sand (Si, SiO₂).

Result from SEM-EDAX analysis shows that the majority of the elements that exist in the foulant sample come from an organic source which is carbon (C) with some amount of Oxygen (O), Sulphur (S) and Iron (Fe). Table 2 shows the weight percentage of the above element in the foulant sample taken from heat exchanger A & B.

<table>
<thead>
<tr>
<th></th>
<th>wt%</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
<td>B</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>69</td>
<td>65</td>
<td></td>
</tr>
<tr>
<td>O</td>
<td>8</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>9</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>7</td>
<td>8</td>
<td></td>
</tr>
</tbody>
</table>

The distribution of carbon will be showed by High Temperature Gas Chromatography (HTGC) up to Carbon 50. Figure 7 shows the results of carbon distribution where the majority of the carbon numbers from 15 to 23.

Table 3. Asphalten Content for Foulant Sample Taken from Heat Exchanger A & B

<table>
<thead>
<tr>
<th>Sample</th>
<th>wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2.2</td>
</tr>
<tr>
<td>B</td>
<td>0.3</td>
</tr>
</tbody>
</table>

DISCUSSION

Past operating data trending for heat exchanger A & B was done to monitor the variation of overall heat transfer coefficient and duty over a period of three years operation between planned shutdowns and relate it to the foulant behavior in the heat exchangers. The fouling trending will be limited by the following:

- Fouling trending will be contributed by a combination of both shell and tube side fouling
- Inaccuracies of the fouling interpretation due to variation of throughput on the shell and tube side

Based on data trending result in Figure 1 and Figure 2, it could be seen that heat exchanger A and B have a different fouling behavior. Heat exchanger A shows a noticeable drop in overall heat transfer coefficient and duty which indicate fouling layer buildup in the heat exchanger over time. Inaccuracies due to the variation of throughput were minimized by comparing the observed trend at the same throughput for shell and tube side. On the other hand, heat exchanger B did not show a noticeable drop in overall heat transfer coefficient and duty and this indicates that fouling is not severe or very minimal in this exchanger.

Visual inspection conducted for both exchangers confirmed the data trending findings above. It could be seen from Figure 5 and Figure 6 that there is a foulant layer...
deposited on the tube sheet and tube internal of heat exchanger A whilst heat exchanger B is relatively clean.

Further investigation was conducted using EXPRESS software to determine the fouling threshold region for heat exchanger A. Figure 3 shows that Ebert-Panchal [5] model prediction fit the measured data very well which is then used to determine the fouling threshold region for heat exchanger A. As shown in Figure 4, the current operating data at the exit of heat exchanger A is well inside the fouling region causing the heat exchanger to foul over time.

It could be said that heat exchanger A and B shows different behavior with regard to fouling propensity. Based on the analysis and observation done for heat exchanger A and B, heat exchanger A tends to foul during operation but fouling is very minimal for heat exchanger B.

To understand the type of fouling, the constituents of the foulant need to be identified. In order to achieve this, an analytical testing is conducted.

Based on the LOI analysis result shown in Table 1, it could be seen that the foulant sample taken are organic in nature with organic portion is more than 80 wt%. So, it is likely that organic/chemical reaction fouling is dominant in these heat exchangers. This is in line with statement in ESDU document [5], “Chemical reaction fouling arising from thermal causes is usually low in the heat exchangers upstream of the desalter, though fouling and plugging due to solids and salt deposition sometimes cause problems. The crude oil becomes hotter as it flows through the pre-heat train, so thermal fouling on the crude side of the exchangers becomes more serious”.

Inorganic analytical testing conducted shows that the compounds exist in the foulant sample are corrosion products (FeS₂, Fe₃O₄), salt (CaSO₄) and sand (Si, SiO₂). Salt and sand are expected to be originated from crude while corrosion products are likely from upstream unit or heat exchanger itself. Result of elemental analysis as shown in Table 2 indicates major portion of the foulant is C element that constitutes the organic compound and also some Fe, O and S element that constitute corrosion products, salt and sand.

For organic analytical testing, HTGC and asphaltene content analysis were conducted for the foulant sample. HTGC analysis result shows that the carbon distribution for the foulant sample is in between C15 – C23. The result as shown in Figure 7 indicates that the carbon distribution is not in the high end region. This might be due to some oil remained in the deposit and the samples are not being rinsed with heptane or other solvent to remove occluded oil before analysis. Asphaltene content analysis result in Table 3 shows that the amount of asphaltene in the mixture is also quite small. The lower asphaltene content could be due to the steam purging as this activities might wash away the upper foulant layer significantly.

WAY FORWARD

Based on the current results of the work performed, there is room for further studies and investigation. When looking at the result of data trending and EXPRESS software simulation, there is a need to revamp the exchanger that falls into the fouling region. This could be done by installing a generating geometry in which fouling can be suppressed (e.g. the use of inserts and alternative baffle type). If the only option left is to operate in the fouling region, optimized cleaning schedule and also good antifoulant program is required so that the effect of fouling could be minimized. Currently there is a project being undertaken by Universiti Teknologi of PETRONAS to come up with an empirical fouling model prediction that will provide a better fouling prediction which enables optimization on the cleaning schedule and antifoulant dosing.

In terms of better understanding the crude behaviour, there is a need to extend the study to look into crude characterization and also crude mixing or crude compatibility study. This will lead to a better fundamental understanding on the fouling mechanism which is very crucial for a better fouling control and mitigation method. Development of test rig is also important for experimental purposes related to the fouling process.

CONCLUSIONS

It could be concluded that organic/chemical reaction fouling has a dominant effect in hot preheat train where the fouling propensity will depend on exchanger geometry, fluid velocity and temperature. Due to the complexity of this issue, further collaborative work needs to be explored.

REFERENCES

[5] ESDU Data Item 3-00016 “Heat exchanger fouling in the preheat train of a crude oil”