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Fouling Characteristic and Tendencies of Malaysian Crude Oils Processing

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Abstract: Hot surfaces of heat exchangers in oil refineries are easily exposed to fouling and it has been a major problem to overcome, particularly in crude preheat train. The crude oils together with their blends have been known to cause significant fouling due to its composition, incompatibility and effect of operating conditions. This study focuses on the composition of fouling deposits with regards to crude oil properties. The study on the asphaltene as fouling contributor was conducted where asphaltene precipitation factors analyzed using Design of Experiment analysis, Taguchi Approach. Besides that, crude oil incompatibility analysis due to asphaltene drop-out using an Automated Flocculation Titrimeter was also conducted. The analyses were conducted for two Malaysian crude oils. Data on crude oil characteristics, asphaltene precipitation and flocculation are presented and the fouling behaviors in Malaysian crude oils are discussed.

Key words: Asphaltene, fouling, taguchi, automated flocculation titrimeter

INTRODUCTION

Fouling of heat exchanger is an unwanted process of accumulation of dirt or growth of deposit on the hot surfaces of heat exchanger. These activities can lead to high pressure drop and reduce flow rates in the system, thus it reducing the heat transfer efficiency of the heat exchanger. Such fouling leads to enormous costs, not only in the cost of loss of energy recovery but also in the loss of product and mitigation measures (Bott, 1995). Mitigation of fouling can decrease the energy demand in fired heater duty, increase the energy recovery with higher throughput as the efficiency of the heat exchanger is optimized and also can lower maintenance cost through a well constructed scheduled cleaning.

Fouling in crude oil is generally believed to be caused by the organic and inorganic impurities of the crude oil itself (Murphy and Campbell, 1992). The crude oil itself is an extreme mixture of various materials and one of the infamous factors governing fouling problem is the crude oils' high asphaltene content. Asphaltene is defined as a component that is insoluble in non-polar solvents such as pentane, hexane or heptane and soluble in solvents such as pyridine, carbon disulphide, toluene or benzene (Watkinson, 1992). Other than asphaltene, traces of metal are always present in petroleum streams as natural compounds and also as corrosion products. For example, certain metals, carbides, oxides and sulfides of V, Fe and Ni are active catalyst for crude oil fouling and could exist in the crude oil preheat train (Satterfield, 1991). Salt of the alkali metal and alkaline earth metal elements

can contribute in crystallization fouling mechanism, especially the inverse solubility salts in the exchangers prior to the desalter. On the other hand, iron sulphide as a corrosion product is second only to asphaltene as the most common foulant in crude pre-heat train (Wiehe, 1999). Since it is a black, granulated solid, it is often mistaken for coke.

Besides the inherent properties and contaminants, crude oil itself plays an important factor as it is blended, or injected with another processing liquid along the processing line. By blending crude oil, it can cause rapid fouling as described by Wilson and Polley (2001) in their research where mixing can create unstable crude solution which can precipitate species such as asphaltene and result in rapid fouling. Mixing typical paraffinic crudes or condensate and asphaltenic crudes can cause the asphaltene to precipitate, giving rise to high fouling factors and this may limit the amount of condensate that can be mixed with the crude oil (ESDU, 2000). Incompatibility of the crude oils can be predicted by laboratory measurement using a distinguish spectroscopic method as demonstrated by Wiehe (1999) and Wiehe and Kennedy (2000). The measurement was conducted by determining the two parameters that used to define crude oil and crude blend solubility; insolubility number, I_N and solubility blending number S_{BN} . Wiehe also stressed on the importance of the blending order since it contributes to the crude oil incompatibility and the procedure was verified commercially in crude preheat train. Saleh *et al.* (2005) studied the effect of mixing and blending crude oils at

certain operating conditions with the intention of using the results to guide a fouling mitigation strategy.

Asphaltene in crude oil: Asphaltene is commonly defined as stated in previous section; however there are many other definitions which have been reported by researchers around the world. Long (1982) reported that the classic definition of asphaltene is the fraction of petroleum which soluble and insoluble in pentane. Nellensteyn (1938) defined asphaltene as the fraction which insoluble in low boiling point paraffin hydrocarbon, but soluble in carbon tetrachloride and benzene and according to Pfeiffer and Saal, (1940) asphaltene is defined as the fraction insoluble in n-heptane but soluble in toluene. Recently, asphaltene is defined by chemists as the part precipitated by addition of low-boiling paraffin solvent such as normal-pentane, and benzene soluble fraction whether it is derived from carbonaceous sources such as petroleum, coal, or oil shale (Mansoori, 2005).

As reported in many literatures, asphaltene is dark brown to black in color which has no definite melting point and when heated, intumescence then decompose and leave a carbonaceous residue. During the analysis, asphaltene can be precipitated out by the addition of a minimum forty volumes of liquid hydrocarbons. If less is added, resin, which is a fraction of crude oil isolated by adsorption chromatography, may appear. This resin appears within asphaltene fraction by adsorption onto the asphaltene.

Being the least understood component in the crude oil, asphaltene is generally high in molecular weight, non crystalline and most polar (Wang, 2000). It consists of polyaromatic condensed rings with short aliphatic chain and heteroatom such as nitrogen, oxygen, sulfur and various known metals. Elemental compositions of isolated asphaltene using excess volumes of n-pentane shows that the amount of carbon and hydrogen usually vary over a narrow range, where $82 \pm 3\%$ carbon; $8.1 \pm 0.7\%$ hydrogen (Speight and Moschopedis, 1980). These values correspond to H/C ratios of 1.15 ± 0.05 . This near constancy values is the cause for general belief that unaltered asphaltene from virgin petroleum have a fixed composition and asphaltene precipitates because of this composition, not only because of its solubility properties. A study by Dickakian and Seay (1988) on the effect of asphaltene on thermal fouling and characterization on deposits formed on the heated surfaces at various times, showed that the deposits were initially precipitated asphaltene which were then carbonized on the surface into an infusible coke. This may be due to the asphaltene have the highest thermal reactivity of any fraction of a crude oil (Wiehe, 1993). While soluble, asphaltene react to form lower molecular weight products but when insoluble the major thermal reaction product is coke.

EXPERIMENTAL

The crude oils used in this study were collected from a local refinery, sealed in proper containers and stored at the temperature below 5°C to reduce the loss of the light component and to prevent oxidation and degradation from exposure to air and light.

The properties of the crude oils were characterized and listed in Table 1. Both crude A and B are paraffinic crude with the density of $\pm 0.8000 \text{ kg}^{-1}$ and viscosity of $\pm 1.0 \text{ cst}$. Crude A however has higher pour point at $+18^{\circ}\text{C}$ as compare to -6°C for crude B. Crude A also has higher percentage of basic sediment, water, ash and most importantly asphaltene content which is more than 3 times higher than crude B. Crude A is expected to have higher fouling tendencies in the processing system based on these inherent properties.

The fouling deposits also collected from a parallel heat exchanger, Exchanger C and D from the same refinery, treated with toluene to remove oil residue and stored at the same condition in opaque glass containers. This is to prevent the possible oxidation or any reaction with normal metal container.

Asphaltene flocculation study using Automated Flocculation Titrimeter (AFT): This equipment is used to measure the compatibility or colloidal stability of asphalt by determining the flocculation onset, point where asphaltene begins to precipitate from a solution of known weight sample. The sample was prepared in a solvent when titrated with a non-solvent or titrant. The analysis complies with ASTM D6703 (ASTM, 2001a).

Crude oil samples, each with different weight were prepared in specially-designed round bottom reaction vials. Toluene was then added to the vials in equal volume producing solution with different concentration of asphalt in solvent. The samples were then kept without any exposure to sunlight for at least 4 hours. before titration can take place. The reaction vial was then placed in the AFT apparatus; in Fig. 1 and titration was conducted using iso-octane (2,2,4-trimethyl pentane). The flocculation points were determined using visible

Table 1: Properties of crude oils used in this study

Properties	Crude A	Crude B
Density at 15°C (kg L^{-1})	0.8021	0.7985
API gravity	44.91	45.70
Pour point ($^{\circ}$)	+18	-6
Viscosity at 100°C (cst)	1.148	1.058
Total sulfur (wt.%)	0.027	0.019
Bs and W (vol %)	0.7	0.1
Ash content (wt.%)	0.007	0.003
Asphaltene content (wt%)	0.139	0.038

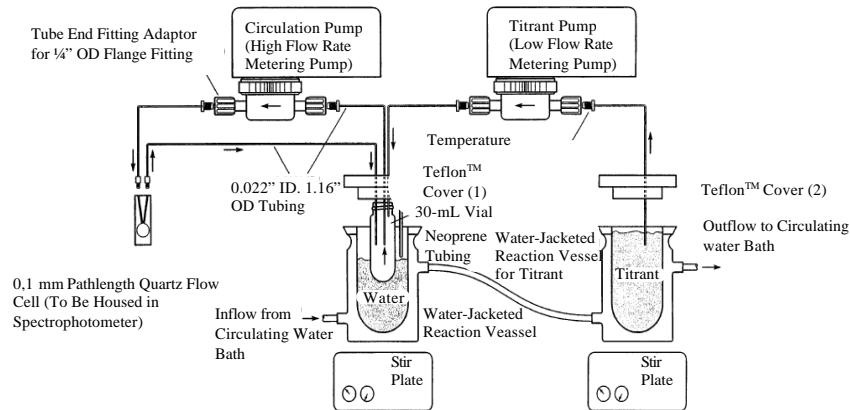


Fig. 1: Flow diagram of AFT

spectroscopy method at a fixed transmittance at 740nm. The onset-point then calculated using the AFTCentral software.

For the present study an indirect method was used to predict crude oil compatibility which was suggested by Saleh *et al.* (2005) using Anderson and Pederson Eq. 1 and Wiehe compatibility model. The solubility values were adapted from ASTM D 6703, where: δ_7 : 8.93 for toluene (solvent) and δ_{10} : 6.99 for iso-octane (titrant). The indirect method was used because the crude oils consists low asphaltene content and it has significant effect on the end point detection. As suggested, a list of high asphaltene crude oils was used as reference:

$$\delta_{cr} = \Phi_0 \delta_0 + \Phi_{10} \delta_{10} + \Phi_T \delta_T \text{ and } \sum \Phi_i = 1 \quad (1)$$

The stability of the oil, a criterion by Wiehe flocculation stability model, δ_f can be written as in Eq. 2, and similarly the oil is stable if the $\delta_0 > \delta_{cr}$. 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 Eq. 3:

$$\delta_f = \Phi_0 \delta_0 + \Phi_{10} \delta_{10} + \Phi_T \delta_T \quad (2)$$

$$S_{BN} = 100 \frac{(\delta_{al} - \delta_{10})}{(\delta_T - \delta_{10})} \quad (3)$$

Asphaltene precipitation study: The method used for the analysis is a derivation from ASTM D3279 (ASTM, 2001b), where insolubility in normal-heptane solvents defines asphaltene which was then determined on a mass percent basis. The analysis was conducted by adding a

Table 2: Sample distribution of asphaltene precipitation study

Exp.	Experimental condition		
	Time (h)	Temperature	Solvent
1	2	25	C ₅
2	2	40	C ₆
3	2	60	C ₇
4	2	80	C ₈
5	14	25	C ₆
6	14	40	C ₅
7	14	60	C ₉
8	14	80	C ₇
9	26	25	C ₇
10	26	40	C ₉
11	26	60	C ₅
12	26	80	C ₆
13	48	25	C ₉
14	48	40	C ₇
15	48	60	C ₆
16	48	80	C ₅

ratio of 100 mL n-heptane per 1g of pre-weighed sample in a flask. The flask was then placed on a magnetic-stirrer hot plate and secured under reflux condition. A period of 15-20 min for reflux is recommended in accordance to the method. The cooled but warm sample was then poured through filter study, GF/D 5.5 cm to filtrate the precipitated asphaltene. Maltenes, the filtrate which contains the saturate, aromatic and resin in a solution was dried in the oven for 15 min at 107°C and the residue is weighed.

Modifications to the analysis were conducted for few parameters, i.e. solvent type, temperature and reflux period to understand the effect of those parameters to asphaltene precipitation behavior. Based on a preliminary result, the study was conducted using Design of Experiment (DOE), Taguchi Orthogonal Array to manage sample and data distribution of the study. Table 2 shows the array that was produced using the approach.

RESULTS AND DISCUSSION

Asphaltene flocculation study using AFT: The compatibility study for every crude oil was conducted with three different concentrations through back titration method where 0.3 mL of reference oil was added. The flocculation solubility parameters of the reference oil were initially identified, and flocculation rate of the asphaltene drop out was plotted against concentration.

Reference oils, H1-H8 used in the study have asphaltene content in the range of 1.35 wt% to 3.10 wt%. The oil solubility parameter, δ_o and flocculation solubility parameter, δ_f of $9.64 \text{ MPa}^{0.5}$ and $8.37 \text{ MPa}^{0.5}$ was respectively obtained for H1 from the titration method. The heavy oil consists of $\pm 5.6 \text{ wt. \%}$ of asphaltene with solubility blending number, S_{BN} of 136.84 and insolubility number, I_N of 70.91. Other similar values for H2-H8 is listed in Table 3. These values then were used in the aforementioned compatibility model equations to get crude oil solubility number.

The solubility blending number, $S_{BN} > 100$ is said to be compatible according to Wiehe and Kennedy (2000), Wiehe *et al.* (2001) and Fig. 2 shows that H2 and H6 are self incompatible crude with S_{BN} value less than 60. H3, H5 and H7 are nearly incompatible crude where S_{BN} is slightly lower than 100. The other two reference oils are believed to be self compatible crude. However this behavior changes as the reference is added to the light Malaysian crude oils.

Based on the information of the reference heavy oil in Table 3, the solubility and insolubility of the Malaysian crude oils were measured. All samples are compatible with the average S_{BN} of 118.29 and 125.27 for crude A and B respectively. Another set of experiment was also conducted to identify potentially incompatible pairs of

Table 3: The solubility parameters for high asphaltene reference oils

Oil Type	H1	H2	H3	H4
$\delta_o(\text{MPa})^{0.5}$	9.64	7.21	8.91	8.49
S_{BN}	136.84	11.21	99.17	77.30
$\delta_f(\text{MPa})^{0.5}$	8.37	7.21	8.18	8.20
I_N	70.91	53.23	61.40	62.54

Oil Type	H5	H6	H7	H8
$\delta_o(\text{MPa})^{0.5}$	8.85	7.97	8.91	9.14
S_{BN}	98.88	50.74	98.97	110.87
$\delta_f(\text{MPa})^{0.5}$	8.30	8.10	8.20	8.33
I_N	67.44	57.18	70.91	69.30

Where, δ_o = Oil solubility parameter, δ_f = Flocculation solubility parameter, S_{BN} = Solubility blending number and I_N = Insolubility number

Table 4: The data of AFT analysis of crude oil blends

	H1*	A8B2	A6B4	A4B6
$\delta_o(\text{MPa})^{0.5}$	9.64	19.09	20.44	20.06
S_{BN}	138.84	119.10	116.86	117.43

* $\delta_f(\text{MPa})^{0.5} = 8.37, I_N = 70.91$

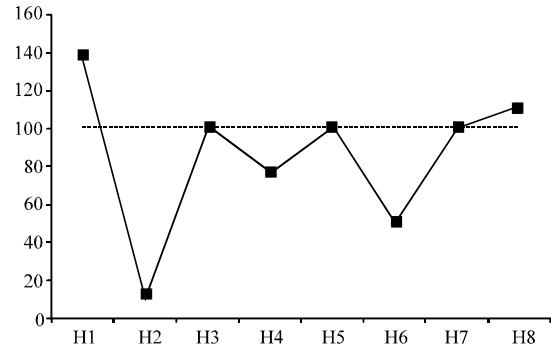


Fig. 2: Graph shows the S_{BN} of the reference oils

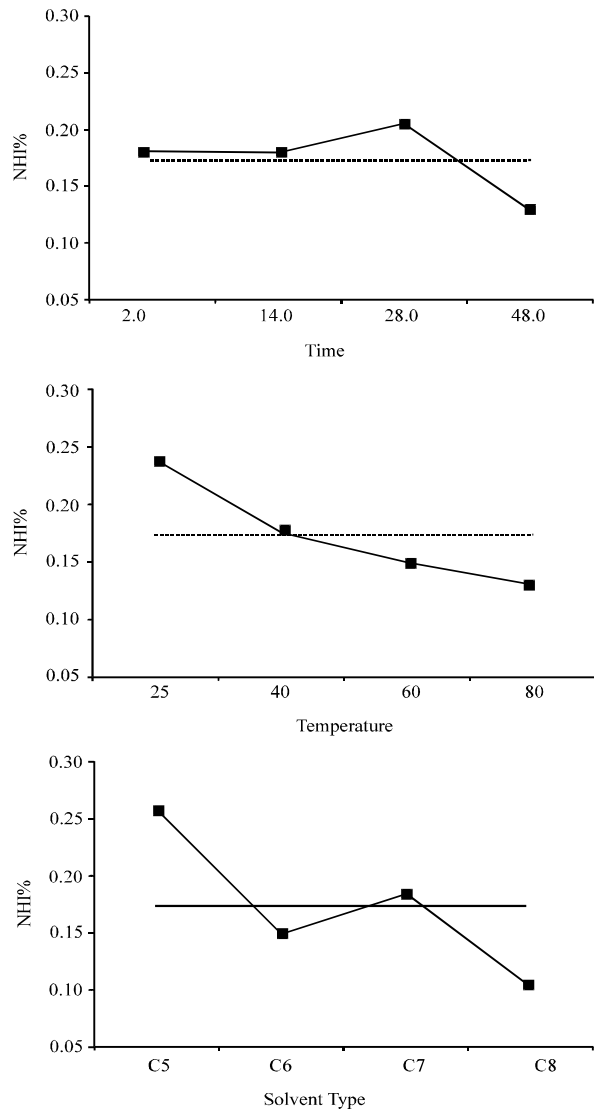


Fig. 3: NHI% of crude A against time (top), temperature (middle) and solvent type, carbon number (bottom) using Taguchi analysis

Table 5: Average NHI% table showing the optimum level and distribution of asphaltene precipitation factors

Level	Time	Temperature	Solvent
Crude A			
1	0.181	0.237	0.256
2	0.179	0.176	0.149
3	0.205	0.150	0.183
4	0.128	0.130	0.104
Average	0.173	0.173	0.173
Optimum	3	1	1
Contribution	0.031	0.064	0.083
Rank	3	2	1
Crude B			
1	0.185 0.207	0.211	
2	0.188	0.143	0.118
3	0.130	0.154	0.195
4	0.099	0.099	0.079
Average	0.151	0.151	0.151
Optimum	2	1	1
Contribution	0.037	0.056	0.060
Rank	3	2	1

Table 6: Analysis of Variance (ANOVA) for asphaltene precipitation in crude A

Factor	S	V	F	S ²	%
Crude A					
Time	0.0123	0.0041	1.451	0.004	3.67
Temp.	0.0259	0.0086	3.054	0.017	16.69
Solvent	0.0492	0.0164	5.800	0.041	39.01
Other	0.0170	0.0028			40.63
Total	0.1045				100.00
Crude B					
Time	0.0225	0.0075	2.178	0.012	10.64
Temp.	0.0237	0.0079	2.295	0.013	11.70
Solvent	0.0474	0.0158	4.598	0.037	32.50
Other	0.0206	0.0034			45.16
Total	0.1142				100.00

Where S = Sum of squares, V = Variance, F = F ratio, S² = Pure sum and % = Percent

studied oils by blending a number of crude oils in different proportions. The test result of the crude blend compatibility can be referred in Table 4 where all the blends are identified to be compatible with each other, in great agreement with the oil mixtures compatibility criterion, where $S_{BN\ mix} > I_{N\ max}$ for the oil mixture to be compatible.

Asphaltene flocculation: The determination of mass percent of asphaltene (insolubility in normal-heptane solvent) is calculated as mass percent of normal - heptane insolubles (NHI %). It is a percentage by weight of the original sample. For percentages of insolubles less than 1.0, it was reported to the nearest 0.01 % and for percentages of insolubles of 1.0 or more; it was reported to the nearest 0.1%.

The data obtained and calculated NHI% of every crude oil was analyzed using DOE Taguchi approach to determine the behavior of asphaltene precipitation with regards to the studied parameters. Fig. 3 shows the precipitation behavior of asphaltene in crude A to the three parameters, where; NHI% is decreasing when

temperature rises, decreasing to the increases of holding time and also decreasing to the increases of carbon number in the solvent used. A very distinguished pattern of drop can be observed in the NHI% response to the temperature. The same behavior was also observed for crude B to all the studied parameters.

Taguchi analysis provides us the contribution level of each parameter to the asphaltene precipitation behavior and ranks them. The highest amount of NHI% is predicted at the optimum level of analysis; a combination of each factor with the highest rank which can be referred in Table 5. From the table, we learned that the optimum level of asphaltene precipitation in crude A is predicted using n-pentane as solvent, 26 h of holding time at the temperature of 25°C producing NHI% of 0.351. The verification was conducted and the actual value of NHI% is 0.364 with 1.3% of deviation. The optimum level of asphaltene precipitation in crude B is using n-pentane as solvent, 12 h of holding time at the temperature of 25°C producing NHI% of 0.304. The prediction NHI% for crude C is 0.297 with 0.7% deviation.

Analysis of variance (ANOVA) is another statistical tool for splitting variability into component sources. These components can be reflected as the signal and the noise where the signal is seen as differences among group means and the noise is seen as variability within groups. By measuring the variability within groups, one has a baseline against which differences among group means can be compared. By comparing the differences based on design of freedom, DOF (n degrees – 1), the F ratio was obtained which indicates the significance of the effect among group mean and later presented in percentage, P (%) which is mentioned in Table 6.

From the analysis, F ratio for solvent type is the highest; meaning solvent type (carbon number) has the greatest effect of asphaltene precipitation with relative influence of 39.01% for crude A and 32.50% for crude B. These values are doubled compared to the other two studied factors. The other or error term, ±41 and ±45% effect response for crude A and B respectively, are quite high considering other contributing factors to the asphaltene precipitation behavior, i.e. excluded factors in the study such as active sulfur content in the crude oil and the content of basic sediment and water (BS and W), uncontrollable factors and also experimental error.

CONCLUSION

All studied crude oils are self compatible and compatible to each other in the range of studied blending ratios. However, blending order wasn't included in the study to fully understand these crude oils compatibility

and it is suggested to be explored in the future work. Asphaltene shows different precipitation behavior for each type of crude oil, and it is highly influenced by the presence of lower molecular hydrocarbon, i.e., pentane, heptane and etc in the crude oil. However, other factors that contribute to the precipitation should also be investigated. Asphaltene also contributes to a certain level of fouling where it precipitates and accumulation of other material could take place on the 'provided site' by the asphaltene. Other properties in the crude oil are still important and contribute to the fouling behavior of a certain crude oil.

Understanding crude oil fouling requires a thoughtful knowledge of its chemistry and its physical deposition mechanisms. With the efforts from this research project, the study could facilitate us to understand the whole fouling process and possibly mitigate.

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