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Relationship Between SARA Fractions and Crude Oil Fouling

¹Chandra Mohan Sinnathambi and ²Norhusna Mohamad Nor

¹FASD, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 31750 Tronoh, Perak, Malaysia

²School of Chemical Engineering, Universiti Sains Malaysia,
14300 Nibong Tebal S.P.S Pulau Pinang, Malaysia

Abstract: The focus of this research is to study the influence of SARA (saturates, aromatics, resins and asphaltenes) fraction on fouling tendencies for four different types of sweet crude oils obtained from a local Malaysian refinery. In view of the great need to improve the energy efficiency of the refining processes and to reduce maintenance cost, crude oil fouling has been the subject of intense research in recent years. A combination of ASTM D3279 and an in-house method using High Performance Liquid Chromatography (HPLC) was established for SARA quantification. The components were then related to the Colloidal Instability Index (CII), ratios of resins to asphaltenes (R:A), calculated from the SARA values and related to the Solubility Number, S_{BN} for each of crude oil. These parameters can be used to mitigate crude oil fouling. A good correlation between CII and S_{BN} was observed.

Key words: Saturates, aromatics, resins, asphaltenes, HPLC technique, fouling

INTRODUCTION

In refinery processing, the qualities of crude oils are the most vital part in determining the cost of refining. Crude oils in general can be divided into three basic categories namely light, medium and heavy. This criterion is based on the composition or fraction derived from crude oil refining. The compositions in general can be classified as light and heavy naphtha, kerosene, gas oil or diesel and residue fractions. Light or sweet crude oils are normally more expensive and have larger amount of low and medium boiling fractions such as naphtha (light and heavy) and kerosene, medium has a higher fraction of kerosene and diesel fuel while the heavy are rich in residue (Wiehe, 2008). Fouling is defined as the formation or deposition of unwanted materials on heat transfer equipment that interfere with the processing of crude oil. This causes an increase in thermal resistance to heat transfers and results in a subsequent loss of equipment efficiency (Wiehe, 2008; Saleh *et al.*, 2005a).

The increment in overall costs of fouling mitigation has been of great concern on refinery processing due to; support cleaning, loss of production during units shut down and elevated operating cost during foulant formation on heat exchanger surfaces. The total cost of all heat exchanger fouling in UK as estimated by Muller-Steinhagen (1995) is around USD 2.5 billion while that in USA it is USD 14 billion. From Nostrand *et al.*

(1981) analysis, they estimated that the cost of fouling in USA is in the order of USD 10 million per annum for a generic refinery processing of 100,000 barrels of crude oil per day on typical refinery operation.

Crude oils can be fractionated into four different components, namely, Saturates, Aromatics, Resins and Asphaltenes (SARA). A reliable compositional characterization of petroleum fractions is important for the optimization of refining processes, products performance evaluation, structure-property correlations, oil-source correlations and environmental issues (Pasadakis *et al.*, 2001).

Chromatographic techniques have been extensively used for hydrocarbons group type determination, such as SARA fractionation. This area of study was first introduced by Jewell *et al.* (1972) where they developed the basis for SARA fractionation. Standard procedure, ASTM D2007 (1993) for SARA fractionation is readily available. However, this technique which is based on clay-gel adsorption chromatography method is lengthy, tedious and laborious as well as expensive to run on routine basis since it requires large quantities of solvents. High Performance Liquid Chromatography (HPLC) methods had been introduced by Suatoni and Swab (1975). HPLC has demonstrated to be a very efficient alternative to the ASTM D2007 (1993) procedures for SARA fractionation since the separation could be achieved rapidly. Further, it is automated and the

techniques are more reproducible. Thus, attempts have been made in the present study to fractionate maltenes (saturates, aromatic and resins) components using HPLC.

Out of the four SARA fractions, asphaltenes play an important role in organic deposition during petroleum production and processing. Issues on asphaltenes and solid precipitation have always been highlighted as one of the major fouling precursors. A small change in Maltenes component or temperature can initiate asphaltene dropouts (Deshannavar *et al.*, 2010).

MATERIALS AND METHODS

The experimental procedures were conducted on four selected sweet crude oil obtained from a local refinery. The experimental methods selected were physical properties which have links to fouling tendencies. The main procedure was the SARA analysis for the fractional determination of asphaltenes and maltenes (saturates, aromatics and resins) content. From this result resins to asphaltene ratio (R:A) and Colloidal Instability Index (CII) were calculated. To support CII results, the solubility number (SBN) using Automated Flocculation Titrator (AFT) was also done. Other physical properties analyses include density, viscosity, pour point, water content and total acid number were also conducted strictly following to American Standard Testing Methods (ASTM).

These physical properties for crude oils characterizations are shown in Table 1. Four types of Malaysian crude oils with API gravity ranging from 30-45 were used in this study.

SARA fractionation: Each crude oil was de-asphalted using ASTM D3279 (1997) to isolate asphaltenes fraction from the maltenes components. The maltenes were isolated to saturates, aromatics and resins using a HPLC unit. The HPLC unit was calibrated under various conditions using Volatile Organic Compounds (VOC) standards supplied by Agilent. The standard mixture consists of 100 µg mL⁻¹ each of n-decane, n-tridecane, n-pentadecane, n-octadecane, toluene, 1,3 diisopropylbenzene, 1-methylnaphthalene and phenanthrene dissolved in n-pentane. For the present study, two 4.6×250 mm µBondapak NH₂ column with 5 µm

packing were used in series with a UV detector operating at a wavelength of 254 nm. This is to monitor elution of each fraction as recommended by Mansoori *et al.* (2007).

The solvents used in this method are n-hexane, dichloromethane (DCM) and iso-propanol (IPA). The maltenes samples were filtered using a 0.2 µm PTFE syringe filter into 1.5 mL glass vial. The maltenes or deasphalted oil collected was then subjected to HPLC separation. In this separation saturates and aromatics were initially eluted while the resins were retained in the column due to its polarity. Dichloromethane was used to recover the resins by column back-flushing method. The system was then cleaned for the next analysis by flushing with iso-propanol for 15 min followed by n-hexane. A stabilize baseline indicates readiness for the next analysis. The chronology of maltenes separation and further fractionation into saturates and aromatics are schematically explained in Fig. 1.

Optimization and calibration of HPLC unit: The HPLC equipment was calibrated by injecting VOC standard with the solvent flow rate of 1.5 mL min⁻¹ as suggested by Fan and Buckley (2002). To optimize the solvent usage a comparison of the separation of components at different flow rates ranging from 0.5- 1.5 mL min⁻¹ was also conducted and is shown in Fig. 2. Optimum peak resolution together with the least amount of solvent used was the target. Multiple injections were also conducted with at least 3 duplications to ensure the repeatability and accuracy of the component’s separation. The resolution

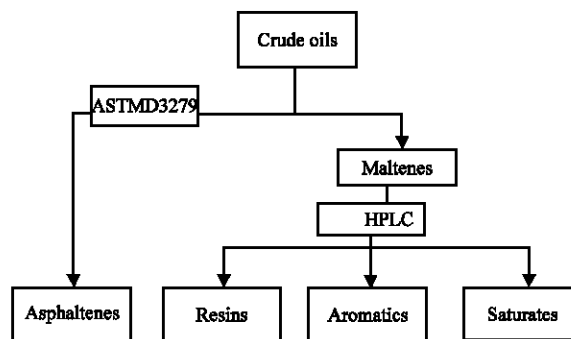


Fig. 1: Schematic of SARA fractionation

Table 1: Properties of Malaysian sweet crude oil

Property	Method	Unit	A*	B*	C*	D*
Density at 15°C	ASTM D5002	kg L ⁻¹	0.7932	0.7872	0.8719	0.8310
API gravity	ASTM D1298	°API	46.89	48.25	30.79	38.78
Viscosity@ 40°C	ASTM D445	cSt	2.35	2.41	3.82	3.01
Pour point	ASTM D97	°C	+12	0	-12	-3
Water content	ASTM D4377	% (m/m)	0.245	0.236	0.145	0.163
Total acid number	ASTM D 664	mg KOH g ⁻¹	0.17	0.19	0.24	0.23

*Due to confidentiality agreement, names of crude oil will not be reveal

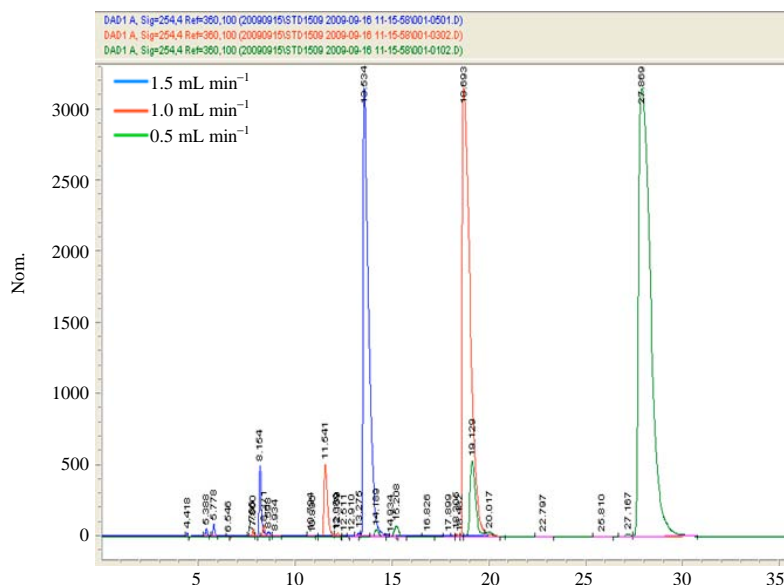


Fig. 2: Comparison of custom VOC standard chromatographs at different flow rates

of the chemicals present in the VOC standards were compared for the best peak resolution. From Fig. 2, it can be seen that the best solvent flow rate is at 0.5 mL min⁻¹.

Solubility number S_{BN} determination: The Automated Flocculation Titrator (AFT) was used in accordance to ASTM D 6703. All four samples selected have less than 0.22 wt.% of asphaltenes. Since, the minimum detection limit for AFT is >0.25 wt.%, an indirect method was used. This method was suggested by both Saleh *et al.* (2005b) using Anderson and Pederson equation (Eq. 1) and Wiehe and Kennedy (2000) compatibility model using heavy oil with high content of asphaltenes as reference. The solubility parameters (δ) were adapted from ASTM (2001), where, $\delta_T = 8.93$ for toluene (solvent) and $\delta_{10} = 6.99$ for iso-octane (titrant). The flocculation rate and other solubility parameters of the reference oil were pre-determined before it is being added to the sweet crude oil sample in accordance with Eq. 1:

$$\delta_{cr} = \phi_o \delta_o + \phi_{10} \delta_{10} + \phi_T \delta_T \text{ and } \sum \phi_i = 1 \quad (1)$$

where, ϕ is the blending wt. while the suffix cr is crude blend, O is ref oil. The oil stability criterion set by Wiehe flocculation stability model, δ_r can be rewritten as in Eq. 2:

$$\delta_r = \phi_o \delta_o + \phi_{10} \delta_{10} + \phi_T \delta_T \quad (2)$$

The oil is considered stable if the solubility parameter (δ) of the crude is higher than the reference crude ($\delta_{cr} > \delta_o$).

For asphaltene stability, the degree of Insolubility number (I_N) must be less than the solubility blending number, S_{BN} (solvency of the oil for asphaltene) which can be calculated as per Eq. 3:

$$S_{BN} = 100 \left(\frac{\delta_{at} - \delta_{10}}{\delta_r - \delta_{10}} \right) \quad (3)$$

Standard experimental procedure is given elsewhere (Deshannavar *et al.*, 2010; Sinnathambi *et al.*, 2011).

RESULTS AND DISCUSSION

Quantification of SARA fractionation: The quantified SARA fractions for crude oil A, B, C and D are summarized in Table 2. The quantified fraction is of concern since 2 different methods were used. To address this concern the mean and standard deviation were calculated to check the accuracy of the results and method. The yield for every sample fractions is quantified gravimetrically. The yield is also used to validate the accuracy of the in-house method. From the results obtained (Table 2) it can be seen that the total yield is >98%. This validates the high accuracy of the in-house method used for SARA quantification.

From Table 2, it can be seen that the major fraction of the four sweet crude oils selected is the saturate fraction ranging between 71-87%, followed by aromatic fraction in the range between 8-24%. The resin fraction on the other hand is much smaller and ranges between 3-5% while asphaltenes, the minor fraction is found to be <0.25%.

Table 2: SARA quantification of sweet crude oils
Concentration (wt.%)

Saturates	Aromatics	Resins	Asphaltenes	Yields 100%
86.62±2.3314	8.600±1.2864	3.15±0.1656	0.12±0.0260	98.49±1.822
80.55±0.8631	14.68±0.8023	3.64±0.5781	0.15±0.0230	99.02±0.540
71.22±1.2023	23.76±0.7801	3.92±0.3296	0.07±0.0208	98.97±0.790
78.79±2.1354	15.37±0.6505	4.18±1.0120	0.22±0.0400	98.56±1.798

Values are Mean±SD

Table 3: The comparison of CII value with SARA

Samples	Saturates (wt.%)	Aromatics (wt.%)	Resins (wt.%)	Asphaltenes (wt.%)	CII
A	86.62	8.60	3.15	0.12	7.38
B	80.55	14.68	3.64	0.15	4.41
C	71.22	23.76	3.92	0.07	2.58
D	78.79	15.37	4.18	0.22	4.04

Even though sweet crude oils have low asphaltene content, this does not mean that it has a lower tendency to precipitate. Various researches have reported that crude oil possessing low asphaltene content can also have higher tendency for precipitation as compared to those with higher asphaltene content (Wiehe, 2008; Deshannavar *et al.*, 2010; Sinnathambi *et al.*, 2011).

Table 3 shows the values for SARA and CII for each of the crude oil analyzed and Fig. 3 illustrates the relationship between SARA fraction and CII values. Since, for all 4 cruds, the CII value is higher than 2, this indicates higher tendencies towards fouling or asphaltene deposition (Bennet *et al.*, 2006; Asomaning and Watkinson, 1999).

Correlation with CII: To understand the interaction between SARA component and fouling formation, Colloidal Instability Index (CII) can be used to determine the tendency of fouling development. CII values for each sweet crude oil were calculated as in Eq. 4:

$$CII = \frac{\text{Saturates} + \text{Asphaltenes}}{\text{Aromatics} + \text{Resins}} \quad (4)$$

Bennet *et al.* (2006) and Asomaning and Watkinson (1999) suggested that crude oils with CII value greater than two have high tendency to foul. Based on the results from Table 3 for the four crude analyzed, crude oil A is most vulnerable to fouling tendency, followed by crude oil B and D (intermediate) and C (lowest). Since, all the 4 crude oils have tendency of being a heavy fouler, the relationship of CII with SARA fractions were plotted and studied. From Fig. 3, it can be seen that increase in saturates and asphaltene fraction, will increase the CII value as observed in crude oil A, B and D, respectively. In contrast with crude oil C which has lower fouling tendency, it has higher aromatic and resins fraction. Consequently, in term of fouling mechanism, this amount of resins and aromatics fraction will help to stabilize asphaltene from micellization or agglomeration, thus preventing fouling (Wiehe, 2008).

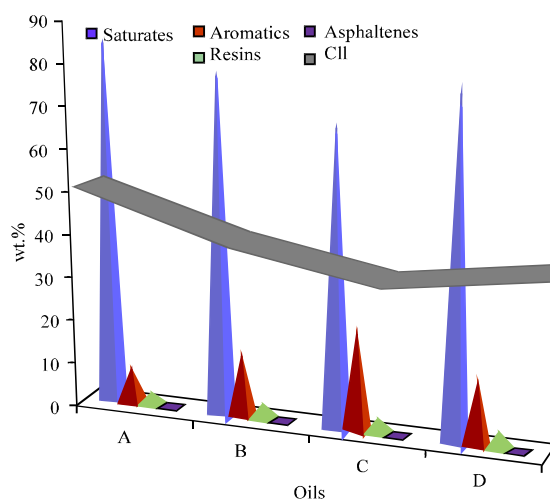


Fig. 3: Comparison of SARA for all crude oils and relationship between CII values

Comparison between resin to asphaltene ratio, solubility parameters and CII: The R:A, S_{BN} and the CII were studied together to understand their behaviors and find a correlation between them. It is generally accepted that resins fraction are natural dispersant of asphaltene in the crude oil (Wiehe, 2008). Higher R:A ratio may indicate higher stability of asphaltene in solution. It should also be noted that higher S_{BN} values also favors higher asphaltene stability. If S_{BN} values >100, it is said to have high compatible factor according to both (Wiehe and Kennedy, 2000; Saleh *et al.*, 2005a). The arbitrary value for S_{BN} <100 indicates that the crude has high tendency to precipitate asphaltene either when mixed or processed individually. A higher CII value on the other hand is undesirable since CII values >2, label the crude as heavy fouler.

From Table 4, it can be seen that S_{BN} and CII values complements each other very well while in the case of R:A ratio the prediction for crude B through D follows the trend except for crude oil A. This anomaly (crude A) needs further studies on the speciation of both resins and

Table 4: Comparison between R/A ratio with S_{BN} and CII

Samples	Resins (wt.%)	Asphaltenes (wt.%)	R:A	S_{BN}	CII
A	3.15	0.12	26.25	113.57	7.38
B	3.64	0.15	24.27	125.27	4.04
C	3.92	0.07	56.00	129.36	2.58
D	4.18	0.22	19.00	120.90	4.41

asphaltenes to gain valuable information on the synergy between the two. In general all the values of S_{BN} and CII value complement each other.

CONCLUSIONS

From the studies, it can be concluded that SARA fractionation was successfully quantified using in-housed developed method using a combination of HPLC for maltenes or SAR fractions and ASTM D3279 (1997) for asphaltene fraction. High recovery of yield greater than 98% for all 4 SARA fractions was realized indicating a strong validation of the in-house method used. Relationship between Colloidal Instability Index (CII), resins to asphaltene ratio (R:A) and Solubility number (S_{BN}) show that all crude oils have tendency for being a heavy fouler. The ascending order for fouling nature of the crude oil can be classified as, cruds $C < D < B < A$.

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