Compatibility Assessment of Crude Oil Blends Using Different Methods

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Today, opportunity crude oils and their blends have attracted the attention of oil companies looking to increase their cross refinery margin. However, when crude oils are blended in the wrong proportions or even the wrong order, they can precipitate asphaltenes (called incompatibility). Once precipitated, it is difficult to re-dissolve asphaltenes quickly. Meanwhile, asphaltenes precipitation is a common problem for oil production companies and refiners and can cause foul preheats exchangers, and catastrophic coking of distillation furnace tubes. If this happens, refineries can lose more than the advantage of purchasing the crude.

This paper focused on possibility of transporting crude oil blends (Sarir, Messla, Nafoura and Amna) through 34 inch Sarir pipeline about 512 km to Hariqha Seaport, prior to blending the crude oils have to be compatible in order to avoid phase out and precipitation of asphaltenes. This work discusses the compatibility of Libyan crude oils as a model system. Various simple techniques were investigated to the determination of insolubility number (I_N) and solubility blending number (S_{BN}) and the prediction of a compatibility scale for two blends. Effect of colloidal instability based on asphaltenes precipitation and SARA composition on fouling was also discussed.

1. Introduction

From the oil well to the refinery, fouling can interfere with the production equipment. It is a common problem for oil production companies and refineries, and periodically process units have to be shut down for mechanical cleaning and maintenance due to fouling resulting in throughput losses or production shutdown. The crude oils and their blends play an important role in increasing refinery profitability, but the risks are high because they are several factors determine the formation of deposits in the pipelines and pipes of heat exchangers, this factors including the percent of contaminates such as inorganic salts, sediments, asphaltenes, waxes, stable emulsions or inorganic solids, and a high metal content Murphy et al, (1992).

These contaminates can cause stable oil-water emulsion problems and leading to high maintenance cost and equipment losses.

Although crude oil fouling is a complex process involving several parallel mechanisms, it is assumed that the organic-derived fouling takes place through the destabilisation of some components of crude oil, their deposition at the tube wall and subsequent degradation to carbonaceous fouling layer Watkinson (1995).

Refiners are currently converting more residual into light fractions, which results in heavy fuels production that contain a higher concentration of asphaltenes. Asphaltenes are components of petroleum, and their behaviour and structure change with temperature, pressure and the composition of oil.

Unwanted asphaltenes precipitation can plug well and distillation equipment and, in many cases, decrease or stop oil production and can further increase the cost of oil recovery processes. Therefore, a detailed knowledge of factors that affect the composition and physic-chemical structure of crude oils is necessary. Asphaltene precipitation during oil production and processing is a serious problem. The economic implications are the significant and can cost millions of dollars. In some cases, fouling problems have been reported to be so drastic that many oil wells have been re-drilled. Asphaltenes are sensitive to shearing forces and electrostatic interactions, and crude distillation and vacuum units often are affected by asphaltene fouling. Crude preheat train and vacuum bottom heat exchangers can plug, and as a result require chemical or mechanical cleaning, otherwise, throughput has to reduced, leading to a loss of production.

Crude selection and compatibility considerations are a critical part of a successful refinery operation. Use of crude compatibility prediction processes and tools can effectively predict the performance of crude oil blends in a specific refinery before they are processed. The compatibility model was developed to predict the proportions and order of blending of oils that would avoid incompatibility Wiehe and Kennedy (2000).

The best strategy for reducing fouling is to use basic knowledge to eliminate its formation.

Fluid catalytic cracking units often report fouling problems in the slurry circulation system, as it happened in Western Europe refinery revamped FCCU and later noticed an increase fouling in the slurry oil exchangers. Several service companies tried to solve the problem by dosing their chemical programmes, but the situation worsened and the financial losses for the unit have been climbed.

2. Structure and analysis of crude oil

2.1 Structure of crude oil

Crude oils are a mixture of many organic compounds, and their overall properties differ from well to well, and broadly classified in to four chemical classes based on differences in solubility and polarity. These components are called Saturates (non solvent), Aromatic (solvent), Resins (dispersant), and Asphaltenes (solute). They represent a wide variety of hydrocarbon molecules that are typically polyaromatic in nature, with some degree of alkyl substitution, and usually contain heteroatom such as oxygen, nitrogen, sulphur and metal atoms in their structures. The blending of oils can significantly change the overall concentrations of SARA at a molecular level, subsequently disturbing the delicate balance and precipitating asphaltenes.

Asphaltenes are very complex molecular and their structure is often desorbed to a compact stack of many thin sheets-like layers. They are suspended by tiny colloidal particles in crude oils. The molecules are stability by natural resins and maintained in the oil due to its stabilisation.

High Asphaltene content means a high conradson carbon residue and a high metal content. Conradson carbon residue is the amount of coke produced in a standard thermal cracking test, and is a measure for potential coke formation at high temperatures.

2.2 Analysis of crude oil

Four Libyan crude oil samples, called S, M, N, and A were selected according to the request from local petroleum company in order to carry out the possibility of transporting these crudes through 34" Sarir pipeline about 512 km to Hariqha Seaport, prior to blending the crude oils have to be compatible in order to avoid phase out and precipitation of asphaltenes. The analysis of crude oil samples were carried out using well recognised standard procedures given in ASTM and IP methods and results are presented in Table-1.

2.3 System overview

The initial hydraulic study show that the pipeline is capable to transfer 300,000 B/D of crude oil in both blends: for blend-1, the study confirmers that the 34" pipeline capable to transfer with flow rate of 235,000 B/D, while the blend-2 can only of transfer 300,000 B/D of crude oil. These crude oils are representing the following blends, for Blend-1 which contains a mixture of (S, M and N) oils and Blend-2 which contains a mixture of (S, M, and A) oils. In this study two blend scenarios are considered.

A Hydraulic study of the 34" crude pipeline from Sarir to Hariqha seaport was carried out to confirm the pipeline capacity at steady state condition within the pipeline maximum allowable operating pressure is 750 psig. The results of hydraulic study show that the pipeline is capable to transfer blend-1 and blend-2. The volume percent and flow rate of each crude oil are summarised in Table-2.

Table 1: Physical properties of crude oils

Description	Crude S	Crude M	Crude N	Crude A
Density@15ºC, g/ml	0.8427	0.8258	0.8305	0.8323
Sp.gravity@60/60 ºF	0.8431	0.8262	0.8309	0.8327
API gravity	36.3	39.8	38.8	38.4
Total sulphur .wt%	0.159	0.188	0.030	0.128
Pour point, ºC	+27	+18	+18	+21
Viscosity@70 ºF,cSt	27.422	13.516	11.735	21.736
Viscosity@100ºF,cSt	13.822	6.0479	5.651	10.621

Table 2: Total production of crude oils

Crudes	Volume % in blend-1	Flow rate in blend-1 B/D	Volume % in blend-2	Flow rate in blend-2 B/D
Crude S	55.0	130,000	55.0	150,000
Crude M	30.0	70,000	22.5	75,000
Crude N	15.0	35,000	------	------
Crude A	------	------	22.5	75,000
Total production	100,000	235,000	100,000	300,000

3. Assessment of the compatibility crude oil blends

3.1 Experimental details

The crude oils and their blends were examined using three different techniques; Turbiscan instrument, Optical microscopy, and SARA test method. All the obtained results were compared to each other to ensure and verify the validity of used techniques.

One of the accurate methods used in this study is Turbiscan instrument Berthod and Hermann (2009) and conforms to modified ASTM D 7061. The Turbiscan MA 2000 technique is based on the principle of multiple light scattering. The intensity of the backscattered light is in direct correlation to the concentration and average diameter of the dispersed phase (particle, droplet and bubble). The instrument has a pulsed infrared source (850 nm) and two synchronic working detector systems. The instrument detects destabilisation phenomena (4-50) times earlier than the naked eye.

In order to carry the compatibility study, each crude oil upon received in stainless steel cylinder and stored at room temperature, then portion of sample was flashed from each crude oil for physical properties and applied by all devices as mentioned above.

3.2 Flocculation tendency

Two blends with defined ratios between S, M, N, and A crude oils were prepared according to the current and expected production scenarios.

Asphaltene stabilization test was conducted for blends using Turbiscan MA2000 according to the standard modified test method describes the analysis in three main steps, which are:

Dilution of crude oil in toluene.

Precipitation of asphaltenes with n-heptane.

Measure stability using Turbiscan instrument.

The Turbiscan instrument is useful for determine the best antifouling or stabilisation additive at the optimal concentration. It is a standard Kurita procedure to optimize the dosing rate of asphaltene dispersants by using Turbiscan technology. The difference between an unstabilised or stabilised sample can be detected quickly with high accuracy.

Any changes in the stability of the sample are detected, which gives an indication of the de-stabilisation process. If the values of flocculation tendency less than 5.0 its mean stable sample, and if greater than 5.0 is normal, and if greater than 10.0 is unstable.

The result of blends shows a high stability reserve i.e. the flocculation tendency was less than 5.0 and can be concluded that to be compatible as Figure1 & 2.
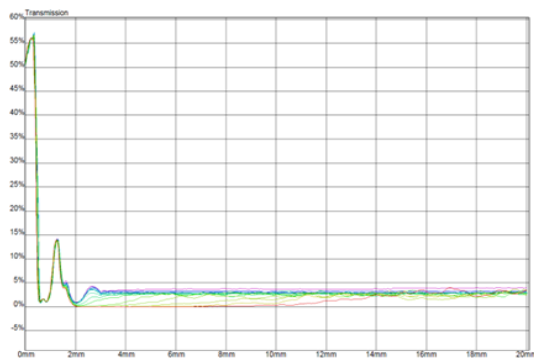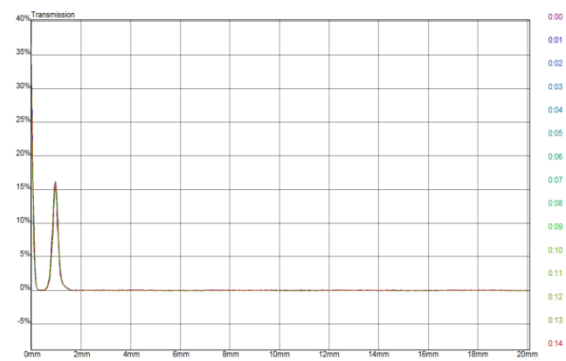

Figure 1: Turbiscan for Blend-1 at 15 minutes   *Figure 2: Turbiscan for Blend-2 at 15 minutes*

3.3 Colloidal instability index analysis

Various criteria describing asphaltene stability and allowing prediction of compatibility have been described in the literature. For example, 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 aliphatic and aromatics. Also introduced a simple colloidal instability index, (CII), Eq(1) based on Saturates, Aromatics, Resins and Asphaltenes (SARA), and this was conducted on the crude oil samples using Clay-Gel (ASTM D-2007). The blending of oils can significantly change the overall concentrations of SARA at a molecular level, subsequently disturbing the delicate balance and precipitating asphaltenes.

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

The CII is expressed as the mass ratio of the sum of asphaltenes and flocculants (saturates) to the sum of (resins and aromatics) in a crude oil. They concluded that blends with CII > 2 tend to be incompatible or unstable, and precipitate asphaltenes. SARA fractionation involves prior separation of asphaltenes from the crude oil by the addition of excess liquid hydrocarbon such as n-pentane or n-heptane (ASTM D4124). Saturates aromatics and resins fractions and then extracted from the de-asphalted oil using liquid chromatography (ASTM D2007). Since blend-2 has the largest amount of asphaltenes, it would be expected to be the most likely to give small rise to measurable rates of asphaltene deposition. The SARA compositions are calculated for two blends along with the colloidal instability index (CII) and the asphaltene to resin ratio (A/R) based on blending ratios. If asphaltenes to resins ratio greater than 0.35 that's mean very unstable. The results are summarised in Table- 3&4 and graphically presented in Figure 3& 4.

Table 3: SARA composition

Composition	Blend-1 wt. %	Blend-2 wt. %
Saturates	64.40	65.70
Aromatics	10.10	11.30
Resins	24.91	22.30
Asphaltenes	0.59	0.70

Table 4: Colloid instability index for crude oil blends

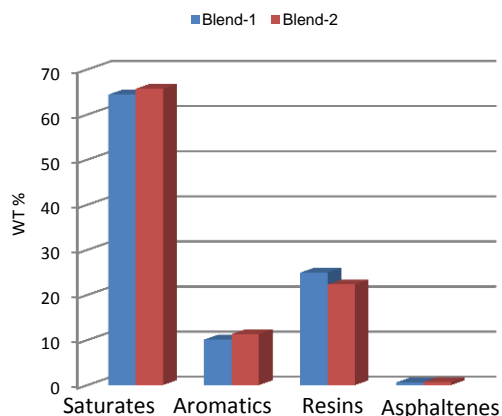| Name	Blend-1	Blend-2
CII	1.85	1.97
A/R	0.024	0.031

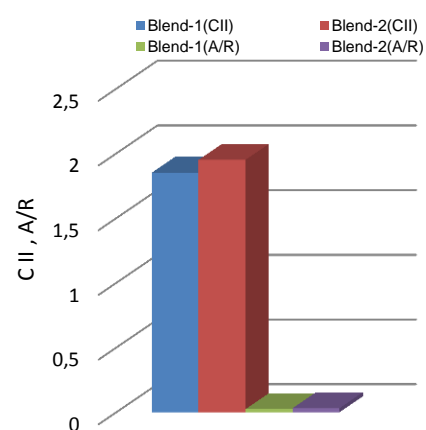Figure 3: SARA composition for two blends

Figure 4: Colloid instability index for two blends

4. Predication of a compatibility model

4.1 Determination of S_{BN} and I_N

Determination of the compatibility or incompatibility of the oils and their blends is the most significant part of this paper. Another method was used and called an optical microscope to determination of flocculation points for oils as well as evidence of asphaltene precipitation. Various mixtures of the solvent were prepared by blending toluene and n-heptane in known proportions, to determine solubility or insolubility for each crude samples. In order to prepare compatible blends of oils, the solubility parameter on a reduce n-heptane-toluene scale is called insolubility number, (I_N). In addition, the tests measures the solubility parameter of the oil that on a reduce n-heptane-toluene scale is called the solubility blending number, (S_{BN}). The determination of (I_N) and (S_{BN}) are key parameters in the prediction of flocculation when dealing with incompatible crude oil blends. The criterion for compatibility of any blend is that the volume average solubility blending number is greater than the maximum insolubility number of any component in the blend ($S_{BN} > I_N$). Where, Insolubility Number, (I_N) measures degree of asphaltene insolubility, while Solubility Blending Number, (S_{BN}) measures ability of oil to dissolve asphaltenes. The (S_{BN}) can be calculated from the following equation:

$$S_{BN}blend = \frac{V_1 S_{BN1} * V_2 S_{BN2} * V_3 S_{BN3} \ldots .* V_n S_{BNn}}{V_1 + V_2 + V_3 \ldots \ldots V_n}$$

(2)

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

$S_{BNmix} > I_{Nmax}$

The model predicts that a particular oil blend is compatible if the maximum (I_N) between the three cruds is smaller than the (S_{BN}) of the mixture, which is the volumetric average of the individual values of (S_{BN}) for each crude oil Wiehe and Kennedy (2000).

The compatibility tests were carried out with S, M, N, and A crude oils. Toluene volume percent in the test liquid is plotted versus 100 times the volume ratio of oil to test liquid. The insolubility number, (I_N) is the y-axis intercept of a line drawn through the two points. The compatibility numbers are measured for the crude oils, the criteria for compatibility of any blend is that the volume average solubility blending number is greater than the insolubility number of any component in the blend. Since the solubility blending number, (S_{BN}) of S crude oil equals to 40.5 is greater than the insolubility number. The solubility blending number of blends of the four crude oils is shown in Figure 5 & 6.

The solubility blending number (S_{BN}) was calculated for each crude oil with the ratio (R), as shown in Table 5, where (R) can be defined as:

$$R = \frac{S_{BN}blend}{I_{Nmax}}$$

(3)

This ratio (R) measures the deviation from incompatibility. When this ratio is less than one, incompatibility is predicted and a value much greater than one is compatible as shown in Table 6.

The compatibility numbers (S_{BN}) and (I_N) was measured for each crude oil, the measurements include:

4.1.1. Heptane dilution test

This involves the determination of the maximum volume of n-heptane (HD) that can be added to a given volume of oil without precipitating asphaltenes. Insoluble asphaltenes are most accurately detected by observing a drop of the mixture between a glass slide and a cover slip under an optical microscope at 100 to 200X. Insoluble asphaltenes are observed throughout the entire view as yellow to brown curved chain agglomerates.

Table 5: Solubility blending numbers and insolubility number for the crude oils

Crude	S_{BN}	I_N
S	40.50	25
M	39.44	34
N	39.68	31
A	34.56	27

Table 6: Solubility blending number and ratio of the blends

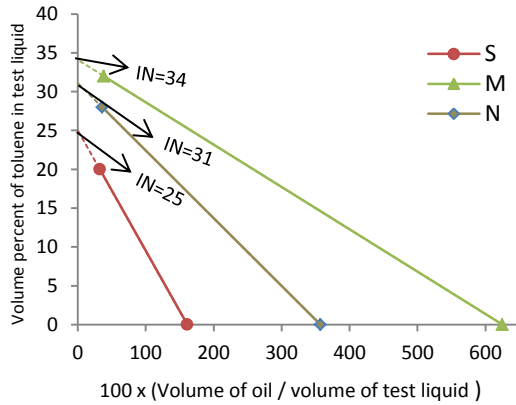| Name	S_{BNmix}	R
Blend-1	40.06	1.17
Blend-2	38.92	1.14

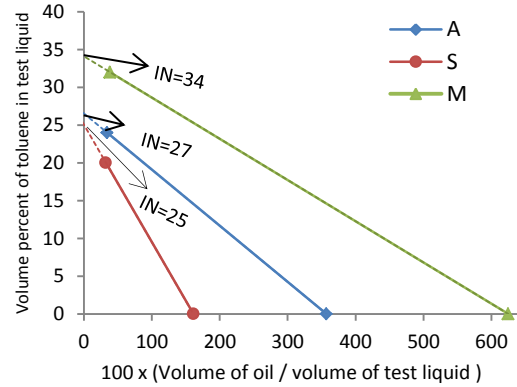Figure 5: Insolubility number for S, M and N crudes

Figure 6: Insolubility number for A, S and M crudes

4.1.2. Toluene equivalence test

The minimum percent of toluene in mixture with n-heptane to dissolve asphaltenes is determined at a concentration of one gram of oil and 5 ml of toluene-n-heptane mixture (test liquid). The volume percent of toluene in the test liquid is plotted versus 100 times the volume ratio of oil to test liquid.

The solubility blending numbers (S_{BN}) for the four crudes were calculated by Eq(4) as follows:

$$S_{BN}=I_N\left[1+\frac{100}{HD}\right]$$
(4)

Where HD is the abscissa intercept or was taken from the heptane dilution test. For self-compatible oils the line slope would be negative, and for self-incompatible oils the x-axis intercepts are infinite, and the S_{BN} equal to the (I_N) and to the percentage of toluene in the test liquid for any volume ratio of oil to solvent mixture. The (I_N) is taken from Figure 5, 6 and the (S_{BN}) is calculated from the mathematical relationship between the parameters. It should be noted that higher (S_{BN}) values favours higher asphaltenes stability.

5. Conclusions

The compatibility study was carried out with crude oil of S, M, N, and A in various proportions. The result of two blends using flocculation tendency shows a high stability and can be concluded that to be stable. Prediction based on S_{BN} parameter was found more than that in the I_N, meaning that the crude oil blends would be compatible. The colloidal instability index also verifies previous results. The three different methods used have demonstrated ensure validity of the techniques and its results. However, there are now a number of suitable analytical instruments and methods in the market. It helps to get a better understanding of the asphaltenes concentration to prevent any fouling and plugging either in pipelines or refineries.

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