

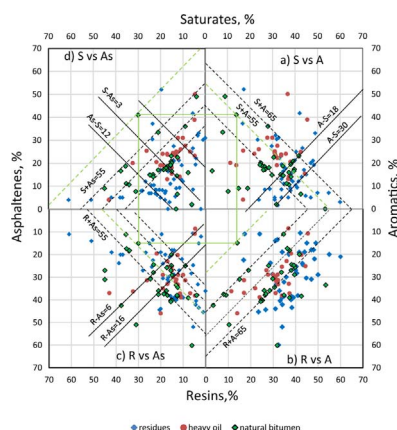
Full Length Article

Relationships between SARA fractions of conventional oil, heavy oil, natural bitumen and residues

Svetlana Rudyk

Oil and Gas Research Center, Sultan Qaboos University, Muscat, Oman

GRAPHICAL ABSTRACT



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ABSTRACT

A number of indices generated from SARA analyses data are used for characterization of petroleum mixtures (e.g. colloidal instability index $I_c = (As + S)/(R + A)$ and asphaltene index $I_a = (As + R)/(S + A)$). Knowledge of relationships between SARA fractions is necessary for selection of indices, understanding of chemical continuum from light to heavy compositions and prediction of properties such as density, viscosity, boiling temperature, asphaltene stability, and others.

SARA analyses data of 230 samples of conventional oil, heavy oil, oil sand, natural asphalt, residues obtained through refinery processes, and bitumen blends from 50 publications are compared. For the exception of conventional oil and bitumen blends, data of SARA fractions taken in pairs follow similar lines with the slopes of $k = \pm 1$ when plotted as Y vs. X for heavy oil, natural bitumen and residues. The slope of 1 indicates that sums or differences of two fractions ($\pm Y \pm X$) are constants regardless of a wide range of variation of Y and X . This allows graphic solution of indices and evaluation whether they are applicable for specific types of petroleum mixtures.

The close values of $(R + A)$ and $(As + S)$ are more often generated for natural bitumen data, relevant to calculation of I_c . For heavy oil and residues, combinations of either $(R + A)$ and $(As + S)$, or $(S + A)$ and $(As + R)$ depend on origin. I_a has no graphic solution for conventional oil.

E-mail address: snr@squ.edu.om.

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1. Introduction

A variety of natural petroleum mixtures are represented by conventional oil and unconventional resources including heavy oil, extra heavy oil, oil/tar sand, shale oil, oil shale, bitumen and asphalt. Petroleum mixtures are also produced after refinery processes. Their definitions are mainly determined by density and viscosity. However, there is no integrity in naming petroleum mixtures [1]. Multiple names are used for similar substances or similar names for different substances. Deposits of bituminous sands are commonly referred to as oil or tar sands. The term asphalt is often used for natural deposits of bitumen. Asphalt is also used to name vacuum residue, the viscous petroleum distillate remained after the atmospheric distillation of crude oil further refined under vacuum. Vacuum residue is also referred to as resid, residuum, vacuum bottoms, bitumen, or topped bitumen [2]. Any blend of vacuum residue is also called residue. Residue is also produced after hydrocracking, thermocracking and catalytic conversion. Natural bitumen and vacuum residues are used for the production of paving grade bitumen, where it essentially acts as a binder for mineral aggregates to form asphalt mixes, also called bituminous mixes, asphalt concrete or bituminous concrete [1]. The grades of bitumen are produced by blending with the addition of polymers.

For the purpose of characterization, petroleum mixtures are separated in SARA (saturates, aromatics, resins and asphaltenes) fractions that are bonded by mutual solubilities. Saturates (S) and aromatics (A) are oily liquids at room temperature. Resins (R) and asphaltenes (As) are dark brown thick viscous liquid to solid.

The saturates fraction is a whitish translucent liquid mainly composed of nonpolar hydrocarbons with linear or branched chains, as well as aliphatic cyclic paraffins. The aromatic fraction, also called naphthene aromatics, is a reddish liquid composed of aromatic hydrocarbons with various degrees of condensation, alkyl-substitution and heteroatom (sulfur, oxygen, nitrogen) content. Aromatics contain compounds with one or more aromatic rings linked to aliphatic chains.

The resin (R) fraction has a higher degree of condensation and heteroatom content than the aromatics [3]. Resins are insoluble in propane and soluble in pentane and higher hydrocarbons. Asphaltenes belong to a class of petroleum macromolecules composed of polycondensed aromatic rings and lateral aliphatic chains. Asphaltenes are insoluble in *n*-alkanes of low molecular weight (*n*-heptane and *n*-pentane) and aromatic soluble (toluene or benzene) [4].

Fractionation of petroleum mixtures into SARA fractions is performed with regard to the polarity of these fractions by using different solvents, eluants and adsorbents. In a first step, asphaltenes are precipitated from petroleum mixture using *n*-heptane [5,6] or *n*-pentane [1]. The deasphalted petroleum mixture can further be investigated for the content of saturates, aromatics and resins by ASTM, HPLC (high-performance liquid chromatography) or TLC-FID (thin layer liquid chromatography coupled with a flame ionization detector (LA-TROSCAN)) methods.

However, SARA procedures and techniques used to wash and filter the precipitants vary widely within testing laboratories. Pentane, heptane, iso-octane, or carbon disulfide are used to precipitate asphaltenes [4]. According to ASTM (e.g. D2007, D4124), deasphalted oil is separated by column chromatography into saturates using *n*-pentane, aromatics using toluene followed by a blend 50/50 with methanol, and resins using trichloroethylene [1]. Normally, resins are the fraction soluble in pentane but insoluble in propane; toluene is only used for the aromatics and pyridine for the resins. Lesuer reviewed that some authors used dichloromethane or 80/20 toluene/*n*-heptane blend for aromatics and 70/25/5 blend of dichloromethane/methanol/isopropanol or 95/5 blend of methylene dichloride/methanol for resins [1].

A number of authors have shown significant difference between SARA results when obtained by ASTM, HPLC or TLC-FID methods [3,7,8]. Investigating SARA compositions of six crude oils by three

different methods, Fan et al. found out that a volatile part consisting of saturates and aromatics were equal to 0 when measured by HPLC but exceeded 37% when measured by TLC-FID. When measured by ASTM, volatiles varied from 2.4 to 16.3% [8]. The difference in the methods, eluant nature, and molecular weight of the solvents significantly affect the relative proportion of each fraction [1,4].

SARA composition is used for the prediction of petroleum properties such as density, viscosity, boiling temperature, shear modulus, biodegradation, coke formation, asphaltene stability and others [4,9,10]. Because four SARA fractions are difficult to compare separately, a number of ratios combining two or more of SARA components have been proposed such as S/A, As/R, (R/As)/(S/A), As/(S + A + R), (R/As + A/S) and others. Gaestel index describing colloidal instability (I_c) is calculated as $(As + S)/(R + A)$, and asphaltene index (I_a) as $(As + R)/(S + A)$ [9,11].

A great variety of petroleum mixtures and the use of a large number of names make their distinction, description and comparison difficult. Though, the petroleum mixtures must be thought of as a chemical continuum with a gradual increase of molar mass, aromatic content and polarity from saturates to asphaltenes [1]. The relationships and interdependence between four SARA fractions influence the correctness of calculated indices and predicted properties.

The objectives of study are to evaluate the types of associations between SARA fractions using data of petroleum mixtures of different types and SARA compositions and determine whether the indices have graphic solutions or they only represent numbers on the coordinate plane. These matters are related to applicability of indices to specific types of hydrocarbon mixtures from light to heavy.

2. Comparison of SARA data

2.1. All data including conventional oil, heavy oil, natural and refinery bitumen, and bitumen blends

SARA data of conventional oil, heavy oil, natural bitumen, residues of refinery processes, asphalt, bitumen blends and binders have been collected from 50 publications [1,3–51]. SARA results have been obtained following the procedures of either ASTM, HPLC or TLC-FID methods. The data containing volatiles are excluded to ensure that the sum of SARA components is equal to 100%.

Six cross-plots using SARA data can be obtained combining S-A, S-R, S-As, A-R, A-As, and R-As, as shown in Fig. 1. The content of S decreases at increasing R content indicating a negative association between two variables. Most of the data are enclosed within a triangle limited by a boundary line described by equation $y = kx + a$ (Fig. 1a):

$$S = -1.33 \cdot R + 100 \quad (1)$$

Accumulations of data along a line (red) parallel to a boundary line (dashed) can also be observed.

Similarly, S decreases at increasing A in Fig. 1b. The data are enclosed within a triangle limited by a boundary line (black dashed) described by:

$$S = -1.16 \cdot R + 100 \quad (2)$$

Similar value of k can be calculated using data presented in [10] that also include data of light oil.

All lines of S/A and R/As must begin from origin (0,0), as shown for example in Fig. 1b and f. At $S/A > 1$, the data are located above, and at $S/A < 1$ below the diagonal line $S/A = 1$ showing the prevailing content of either S or A. On visual observation, there are no accumulations of data along the lines starting from origin. Accumulations of data can be observed along the lines with either positive or negative slopes. For example, data follow a line parallel to the boundary line (orange), a line intercepting A-axis at 45% (red) or a line with a positive slope (blue). Hence, ratios of S/A and As/R may not reflect the continuity of changes from conventional oil to bitumen because the data

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