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Characterization of Pure and Undefined Petroleum Fractions of Messla and Sarir Crude Oils of Libya Using Correlation Models

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ABSTRACT

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Knowing the physical properties of hydrocarbons and petroleum fractions is essential for designing most crude oil production and refining processes. Several correlations, called group contribution methods, have been proposed in the literature to assess these parameters and have been used extensively. The majority frequent correlations reported in the literature, where it is generally accepted in the petroleum industry, are used to describe unspecified fractions of oil. The only input parameters required are specific gravity and normal boiling point or molecular weight. Calculated properties include: normal boiling point (T_b), Molecular weight (Mw), critical properties for instance critical pressure (P_c), critical temperature (T_c), critical volume (V_c) and acentric factor (ω), as well as other parameters including Watson factor (K), and compressibility factor (Z_c). In this approach, x samples of petroleum fractions of Messla and Sarir crude oils of Arabian Gulf Oil Company, Libya have been collected. A quantity of characterization technique of untainted and unknown petroleum fractions have been presented to foresee the physical properties of these petroleum fractions. Correlations for characterizing non-specific petroleum fractions suppose precise seriousness and boiling point as input parameters. These correlations are Twu Correlations, Cavett Correlations, Kesler-Lee Correlations and Riazi-Daubert Correlations. The physical properties of the compounds in terms of specific gravity (γ) and (T_b) were shown on the algorithm and the correlation models for the auxiliary acids were corrected in this study. The considerations addressed revealed that there is no significant difference between the correlation models and the results obtained and it appears to be very close to the similar published data of the cited authors.

Keywords: Correlation Models, Petroleum Fractions, Physical Properties, Hydrocarbons Characterization.

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I. INTRODUCTION

Petroleum restrains severe variety of organic functionality and molecular size. Crude oils and refined petroleum products, in particular, are largely composed of hydrocarbons, which are chemicals made up of only hydrogen and carbon in different molecular configurations. Crude oils include hundreds of diverse hydrocarbons and other organic and inorganic stuffs counting atoms of sulfur, nitrogen, and oxygen, in addition to metals for instance iron, vanadium, nickel, and chromium [7] , [15]. On the other hand, Petroleum is a fluid, gaseous, or constant natural solid mixture, mainly composed of hydrocarbon fractions, to facilitate accrues in underground tanks. Since a generic expression with the purpose of is constantly changing over time [1], it is generally lengthy and costly. Therefore, one frequently searches for empirical correlations, derived from the input of two or more characterizing factor [10]. Knowledge of the physical, chemical and thermodynamic properties of petroleum mixtures play an important role in the design and operation of almost every part of equipment in the petroleum industry. In chemical processes, it is needed to know these data to improve the efficiency of equipment and optimize time and energy consumption. Some physical properties of mixtures are easily measurable, such as specific gravity, while other properties such as the critical properties and enthalpy of vaporization cannot be measured easily [5].

The constituents of a natural reservoir fluid form an almost continuous hydrocarbon spectrum from the lightest, (methane), throughout intermediate molecular weights (butane, propane) and up to a very large molecules (hexane plus). The relative proportion of these different components can vary in a large range, which results in petroleum fluids showing very different features. For instance, the simplest reservoir fluids are natural gas, while the most complex molecular mixtures are those of black oil and bitumen [17]. The chemical and physical properties of petroleum gases and liquids are stressed, particularly their phase behaviour under subsurface conditions which is shown to be a very important factor in determining migration behavior.

The physical properties of a petroleum fluid are determined by its composition; moreover, many of these hydrocarbons vary significantly as a function of temperature and pressure. Petroleum reservoirs have temperatures that vary from ambient to more than 200°C and a pressure that can be as high as 150 MPa [17],[10]. The reservoir conditions depend on the depth of the reservoir and on the geological processes that the reservoir has experienced since it was contained the reservoir fluid [17].

The computational approach for studying physicochemical properties of heavy petroleum factions have been studied by Tovar, et al., [14 cited in 15] as their result suggested that the computational approach is a powerful and an efficient tool for predicting the properties of petroleum fractions. Their method required Boiling Temperature curve, and the specific gravity, as the input data information. This method focuses specifically on heavy fraction and selection of a right characterization method for petroleum fraction has an important effect on calculated properties [14 cited in 15]. To sum up, the classification of petroleum and natural gas as naturally occurring mixtures of hydrocarbons occurs by virtue of the fact that they can be separated into their original hydrocarbon constituents that have not been altered by any applied process. The hydrocarbon constituents, separated from petroleum and natural gas, are the hydrocarbon constituents that existed in the reservoir.

II. PHYSICAL PROPERTIES OF PETROLEUM CRUDE OIL

The physical properties of crude oils are the quantitatively measurable characteristics of crude oils. They vary according to the composition of the oil, the relative abundance of the groups of hydrocarbons, and essentially depend on reservoir temperatures and pressures [8]. Physical properties can be observed or measured without changing the composition of matter. Physical properties are used to observe and describe matter. Physical properties that are of interest in the current context include: boiling point, melting point, density, vapor density, flash point, ignition temperature, and dew point [18].

Petroleum exhibits a wide range of physical properties and several relationships can be made between various physical properties [17]. Whereas properties such as viscosity, density, boiling point, and color of petroleum may vary widely. Coupled with the changes brought about to the feedstock constituents by refinery operations, it is not surprising that petroleum characterization is a monumental task [9].

Petroleum refinery processes can be conveniently divided into three different types:
1) Separation: division of the feedstock into various streams (or fractions) depending on the nature of the crude material
2) Conversion: that is, the production of saleable materials from the feedstock by skeletal alteration, or even by alteration of the chemical type of the feedstock constituents
3) Finishing: purification of the various product streams by a variety of processes that remove impurities from the product [9].

Physical properties of the almost limitless variety of crude oils are generally correlated with aspects of chemical composition.

III. CHEMICAL PROPERTIES

The chemical properties of crude oils vary in relation to changes in geotemperatures and pressures, variations occurring at all times within the oil pool. Some of the chemical properties are related to the origin, migration, and accumulation of the crude oil [8], coupled with some other elements of katagenesis. Such chemical properties as paraffin wax and perhyrins are complex forms of hydrocarbons which have genetic relationship with living organic-life [1]. Occurrence of isoprenoid hydrocarbons, such as pristanes and phytanes in crude oils, enhances the construction of the genetic environments of deposition of the source rocks. Trace metal substances concentrated in crudes are thought to be derived from sea water as secretions by marine life [8].

IV. PETROLEUM FLUIDS COMPOSITION

The most important influences on the compositions of petroleum fluids are:

- The depositional environment of their source rocks;
- The temperature at which they were expelled from their source rocks, and
- Biodegradation and phase transformations after they have left their source rocks.

In many cases, the composition of a petroleum sample may allow the depositional environment of its source rock, and its temperature history (before and after expulsion) to be determined. This information assists the search for more petroleum in a region [25].

Two determine composition of the petroleum fluids are quantitative and qualitative chemical analysis) have to be known. For a hydrocarbon with a given molecular formula C_xH_y, the number of possible isomers increases dramatically as the molecule becomes larger. Even for the paraffins in the C_5-C_{12} range, the number of possible isomers is greater than 600, around 200-400 of which have been experimentally observed [1].

V. CHEMICAL COMPOSITION

Composition refers to the specific mixture of chemical compounds that constitute petroleum. The composition of these materials is related to the nature and mix of the organic material that generated the hydrocarbons [9]. Crude oils are made up of liquid paraffin hydrocarbon compounds ranging from pentane to pentadecane (C5 – C15). All crude oils contain some appreciable amount of the naphthene compounds, (10% by composition). Crude oils also contain a great variety of heteroatomic chemical constituents, comprising of sulphur, oxygen, carbondioxide, nitrogen and trace metals. Nitrogen varies from 0.01 to 2% as dissolved gas in the crude oil [8].

The chemical composition of petroleum is largely speculative due to the difficulty of a complete identification caused by the enormous number of components [1]. Gases produced from a petroleum reservoir mainly contain alkanes lighter than heptane, with methane and ethane being the predominant components [17]. However, in addition to the hydrocarbons, light non-hydrocarbons compounds including nitrogen, carbon dioxide, and hydrogen sulphide are also present with their proportions are being related to the reservoir originally originated. The composition of petroleum obtained from the well is variable and depends not only on the original composition of the oil in situ but also on the manner of production and the stage reached in the life of the well or reservoir [9].

Crude oils are characterized by some physical and chemical properties, which to a measurable extent, play important role in the understanding of the oils geologic nature and environment of origin, such a physical property as optical activity is dependent on hydrocarbon derivatives from organic cholesterine substances, and are destroyed at high temperatures of about 2000C. They serve as important tools for environmental analysis, reconstruction of temperature history of the oil, and correlation of crude oils of similar geologic ages [8].

Petroleum crude oil, contains larger hydrocarbon molecules with its appearance, composition, and other properties (e.g. heptane plus) vary largely with different petroleum reservoirs. Nevertheless, nearly all naturally occurring petroleum liquids have fairly narrow limits of elemental composition with varying values of percentage weight including: Carbon: (83.0-87.0%) , Hydrogen: (10.0-14.0%) , Nitrogen:

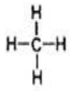
(0.1-2.0%), Oxygen: (0.05-1.5%), Sulfur: (0.05-6.0%) [17]. Both the physical nature and chemical composition of petroleum are determined initially by the type of organic matter in the source rock where the petroleum is generated [4].

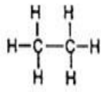
VI. HYDROCARBON COMPONENTS

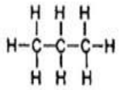
Due to its origin, crude oil is a complex mixture containing thousands of different hydrocarbons [19] that can be separated into a variety of different generic fractions by distillation .And the terminology of these fractions has been bound by utility and often bears little relationship to composition. The major components of petroleum are hydrocarbons, compounds of hydrogen and carbon that display great variation in their molecular structure. The simplest hydrocarbons are a large group of chainshaped molecules known as the paraffins [9]. The majority of hydrocarbons found naturally occur in crude oil, where decomposed organic matter provides an abundance of carbon and hydrogen which, when bonded, can catenate to form seemingly limitless chains [18].

The hydrocarbon components of petroleum are commonly accepted to group the different compounds present in crude oils in different families according to their chemical structure (paraffins, naphthenes and aromatics) or polarity (saturates, aromatics, resins and asphaltens) [9]. Olefins (also called alkenes) are so scarce in naturally occurring petroleum that they may be neglected.

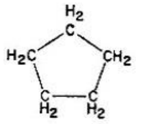
Paraffins, called alkanes or known as acyclic alkanes and have the general formula of C_nH_{2n+2}, where n is the number of carbon atoms in a given molecule. Paraffins are divided into two groups of normal and isoparaffins. Both normal and isoparaffins have the same molecular formula C_nH_{2n+2}. the open formula for n-butane, n-C_4, can be shown as CH_3-CH_2-CH_2-CH_3, based on the quadrivalency of the carbon atom, and for simplicity, only the carbon-carbon bonds are drawn and most C-H bonds are omitted, for more explanation, methane (CH_4), ethane (CH_3CH_3), propane ($CH_3CH_2CH_3$) are saturated hydrocarbons with straight (normal paraffin) or branched (isoparaffin) chains, but without any ring structure. Paraffins are the largest series of hydrocarbons found in petroleum and beginning with the simplest compound, methane.

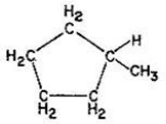

Methane

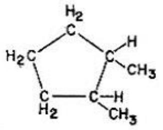

Ethane


Propane

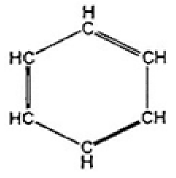
Naphthenes, also recognized as cycloalkanes or alicyclic hydrocarbons, are rings or cyclic saturated hydrocarbons with a general formula of $(C_nH_{2n5}H_{10})$, such as cyclopentane (C_5H_{10}), methylcyclopentane ($C_5H_9CH_3$), dimethylcyclopentane ($C_5H_8CH_3CH_3$), and their derivatives such as n-alkylcyclopentanes are normally found in crude oils, and are saturated hydrocarbons containing one or more rings, each of which may have one or more paraffinic side chains. Naphthenes are present in all fractions in which the constituent molecules contain more than five carbon atoms.

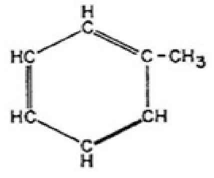

Cyclopentane


Methylcyclopentane


Dimethylcyclopentane

Aromatics, The simplest aromatic hydrocarbon is benzene (C_6H_6) toluene ($C_6H_5CH_3$) containing at least one benzene ring. Aromatic hydrocarbons are an important series of hydrocarbons found in almost every petroleum mixture from any part of the world. Aromatics are cyclic but unsaturated hydrocarbons with alternating double bonds. Many of the aromatic hydrocarbons in petroleum consist of aromatic and naphthenic rings and bear normal and/or branched alkane side chains. Under standard conditions, benzene, toluene, and xylene are in liquid form whereas higher aromatics such as naphthalene occur as solids in isolation, but dissolve to form a liquid solution with simple aromatics.


Benzene


Toluene

VII. PHYSICAL PROPERTIES OF NARROW DISTILLATION CUTS AND THEIR CHARACTERIZATION

Characterization of crude oil is an important step in the application of equations of state for pressurevolume-temperature (PVT) predictions and phase behavior calculations. Such calculations are needed in reservoir simulation or in the design and operation of refinery distillation columns.

The compositional analysis of petroleum fractions can't provide the necessary information for all of the real components in a petroleum mixture. The compositional information obtained varies with boiling point range [16]. Hydrocarbon components up to C_6 and non-hydrocarbon gases including (N_2, CO_2 and H_2S) can be quantified discretely and the properties of these well-defined components are readily found in literature review. The low boiling range in the C_{7+} fractions (e.g. up to C_{30}) can be fractionated in terms of narrow TBP fractions and their molecular weights and specific gravities can be experimentally determined. For the heavy end of the C_{7+} fractions, and TBP residue, there was no further analysis of their molar distribution is made and only the molecular weight and specific gravity of the whole residue are experimentally determined. The only available information about the C_{7+} fraction is its molar composition, specific gravity and molecular weight [16].

The properties involved in the characterization of petroleum hydrocarbon fractions include the molecular weight, (M_w), normal boiling point (T_b), the specific gravity(γ), critical temperature (T_c), critical pressure (P_c), and the acentric factor ω[13].

For a pure component, the critical point is the point that terminates the vapour pressure curve, while the critical temperature (T_c) is the highest temperature at which the substance can exist simultaneously as vapour and liquid. Therefore, at temperatures above T_c there is no phase transition can occur between vapour and liquid. For pure components, T_c can be measured in principle and compilations of T_c are readily available [13],[14].

Similarly the critical pressure (P_c) of a pure component is the highest pressure at which the pure component has a vapour liquid phase transition or it is the highest possible vapour pressure of the component. For the same reasons explained above for the critical temperature, the critical pressure cannot be measured for large hydrocarbon molecules [14].

VIII. MATERIALS AND METHODS

The Messla oil field is the most recent addition to the list of 20 giant fields discovered within the prolific Sirte basin of Libya. The field is located in the southeastern portion of the Sirt Basin, north central Libya, approximately 500 Km Southeast of Benghazi and 40 Km Northwest of the Sarir Oil Field Figures 1and 2.

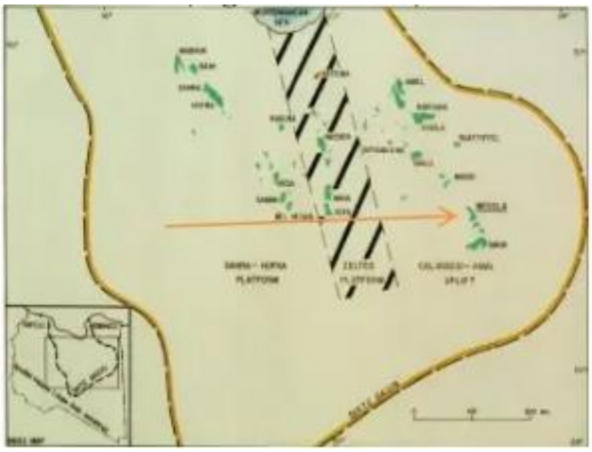


Fig. 1: location of Messla Oil Field (orange arrow)

Fig. 2 Index map southeast Sirt basin showing location of Sarir and Messla fields, broad basement highs (BC), and concession boundaries [11].

Properties of physiochemical for instance definite gravity, API gravity, Reid vapour pressure, pour point, initial and final boiling points acidity, salt content sulphur content etc. of petroleum crude oil and petroleum fractions are determined through the data of chemical analysis which carried out on the Messla and Sarir crude oils samples and petroleum products in Tobruk refinery of Libya using different analytical technique as ASTM D86 technique. These properties are used in correlation models to predict the other properties of petroleum fractions [6]. When used with the ASTM viscosity chart (or its analytical equivalent), the new correlation provides a method for the prediction of viscosity-temperature behavior of fractions from the Watson characterization factor and specific gravity.

IX. CORRELATION MODELS

1. Cavett Correlations

A. Molecular weight, MW

The molecular weight, of the investigated samples can be calculated using (Soreide Correlation) (f(MW)) using Equation (1):

$$f(MW) = 1071.28 - 9.417 \times 10^{4} MW^{0.03522} SG^{3.266} exp(-4.922 \times 10^{-3} MW - 4.7685 SG + 3.462 \times 10^{-3} MWSG) - k = 0 \tag{1}$$

where

$T_b = 1.8k$ (2)

K is Watson characterization factor, Mw is the molecular weight, and SG is the specific gravity.

B. Normal Boiling Point (Soreide Correlation)

The normal boiling point can be calculated using Equation (3) as following:

$$k = 1071.28 - 9.417 \times 10^{4} MW^{0.03522} SG^{3.266} exp(-4.922 \times 10^{-3} MW - 4.7685 SG + 3.462 \times 10^{-3} MWSG) = 0 \tag{3}$$

C. Critical Temperature

The critical temperature can be calculating by applying Equation (4):

$$T_c = 1.8[426.7062278 + 0.95187183F - 6.01889 \times 10^{-4} F^2 - 4.95625 \times 10^{-3}(API)F + 2.160588 \times 10^{-7} F^3 + 2.949718 \times 10^{-6}(API)F^2 + 1.817311 \times 10^{-8}(API^2)F^2] \tag{4}$$

D. Critical Pressure

$$P_c = 14.5038 \times 10\text{^}[1.6675956 + 9.412011 \times 10^{-4} F - 3.047475 \times 10^{-6} F^2 - 2.087611 \times 10^{-5}(API)F + 1.5184103 \times 10^{-9} F^3 + 1.1047899 \times 10^{-8}(API)F^2 - 4.8271599 \times 10^{-8}(API^2)F + 1.3949619 \times 10^{-10}(API^2)F^2] \tag{5}$$

E. Critical Volume (Reidel Correlation)

$$V_c = \frac{10.732\, T_c}{MWP_c[3.72 + 0.26(5.811 + 4.919\omega - 7)]} \tag{6}$$

where

$$API = \frac{141.5}{SG} - 131.5$$

$$F = T_b - 459.67 \quad (7)$$

F. Acentric Factor (Korsten's Correlation)

$$\omega = 0.5899 log\left[\frac{P_c}{14.696}\right] / \left[\left(\frac{T_c}{T_b}\right)^{1.3} - 1\right] - 1 \quad (8)$$

2. Twu Correlations

Twu (1984) **[21]** used the critical properties from back-calculated to obtain his correlations for undefined petroleum fractions as following:

A. Critical Temperature

$$T_c = T_c^0[(1 + 2f_r)/(1 - 2f_r)]^2 \quad (9)$$

where

$$T_c^0 = k/(0.533272 + 0.34383 \times 10^{-3}k + 2.52617 \times 10^{-7}k^2 - 1.65848 \times 10^{-10}k^3 + 4.60773 \times 10^{24}k^{-13}) \quad (10)$$

$$f_r = \Delta SG_T\left[-0.27016/k^{0.5} + \left(0.0398285 - \frac{0.706691}{k^{0.5}}\right)\Delta SG_T\right] \quad (11)$$

$$\Delta SG_T = exp[5(SG^0 - SG)] - 1 \quad (12)$$

$$\Delta SG_T = 0.843593 - 0.128624\alpha^{12} \quad (13)$$

$$k = T_b/1.8 \quad (14)$$

$$\alpha = 1 - (k/T_c^0) \quad (15)$$

B. Critical Volume

$$V_c = V_c^0[(1 + 2f_V)/(1 - 2f_V)]^2 \quad (16)$$

where

$$V_c^0 = (0.34602 + 0.30171\alpha + 0.93307\alpha^3 + 5655.414\alpha^{14})^8 \quad (17)$$

$$f_V = \Delta SG_V\left[0.347776/k^{0.5} + \left(-0.182421 + \frac{2.248896}{k^{0.5}}\right)\Delta SG_V\right] \quad (18)$$

$$\Delta SG_V = exp[4(SG^{0.2} - SG^2)] - 1 \quad (19)$$

C. Critical Pressure

$$P_c = P_c^0(T_c/T_c^0)(V_c^0/V_c)[(1 + 2f_P)/(1 - 2f_P)]^2 \quad (20)$$

where

$$P_c^0 = (1.00661 + 0.31412\alpha^{0.5} + 9.16106\alpha + 9.5041\alpha^2 + 27.35886\alpha^4)^2 \quad (21)$$

$$f_P = \Delta SG_P \left[\left(2.53262 - \frac{34.4321}{k^{0.5}} - \frac{2.30193k}{1000}\right) + \left(-11.4277 + \frac{187.934}{k^{0.5}} + \frac{4.11963k}{1000}\right)\Delta SG_P\right] \quad (22)$$

$$\Delta SG_p = exp[0.5(SG^0 - SG)] - 1 \quad (23)$$

D. Molecular Weight

$$Mw = exp\{\beta[(1 + 2f_M)/(1 - 2f_M)]^2\} \; (24)$$

$$f(\beta) = exp\left(5.12640 + 2.71579\beta - 0.286590\beta^2 - \frac{39.8544}{\beta} - \frac{0.122488}{\beta^2}\right) - 13.7512\beta + 19.6197\beta^2 - k = 0 \quad (25)$$

$$f_M = \Delta SG_M[x + (-0.0175691 + 0.143979/k^{0.5})\Delta SG_M] \quad (26)$$

$$x = |0.012342 - 0.244541/k^{0.5}| \quad (27)$$

$$\Delta SG_M = exp[5(SG^0 - SG)] - 1 \quad (28)$$

E. Critical Compressibility Factor

$$Z_c = \frac{P_c V_c}{RT_c} = \frac{P_c V_c}{83.14T_c} \quad (29)$$

F. Acentric Factor (Edmister's Correlation)

$$\omega = \frac{3}{7} log\left[\frac{P_c}{1.01325}\right] / \left[\left(\frac{T_c}{k}\right) - 1\right] - 1 \quad (30)$$

3. Riazi-Daubert Correlations

Riazi and Daubert (1987) [15] developed a set of equations to evaluate properties of undefined petroleum fractions. Given specific gravity (SG) and boiling point (T_b) or molecular weight (Mw) of the petroleum fraction, physical properties are estimated as follows:

A. Molecular Weight (Mw)

If specific gravity (SG) and boiling point (Tb) of the petroleum fraction are given, molecular weight (Mw) is estimated as follows:

$$Mw = 42.965k^{1.6007} SG^{4.98308} \exp\left(2.097 \times 10^{-4}k - 7.78712SG + 2.08476 \times 10^{-3}kSG\right) \quad (31)$$

Where

$$k = \frac{T_b}{1.8} \quad (32)$$

B. Normal Boiling Point (NBP)

In case boiling point (T_b) of the petroleum fraction is not known and molecular weight (Mw) is given instead, the above equation is rearranged and solved iteratively for k. The objective function for the nonlinear solver is given by:

$$f(k) = 42.965k^{1.26007}SG^{4.98308}exp\ (2.097 \times 10^{-4}k - 7.78712SG + 2.08476 \times 10^{-3}kSG) - MW = 0 \qquad (33)$$

C. Critical Temperature (T_c)

$$T_c = 17.14194k^{0.8107}SG^{0.33691}\exp\ (-9.314 \times 10^{-4}k - 0.544442SG + 6.4791 \times 10^{-4}kSG) \qquad (34)$$

D. Critical Pressure (P_c)

$$P_c = 46.35124404 \times 10^5 k^{-0.4844}SG^{4.0846}\ \exp\ (-8.505 \times 10^{-3}k - 4.8014SG + 5.749 \times 10^{-3}kSG) \qquad (35)$$

E. Critical Volume (V_c)

$$V_c = 9.689574 \times 10^{-4}k^{-0.7506}SG^{-1.2028}\ \exp\ (-2.64222 \times 10^{-3}k - 0.26404SG + 1.971 \times 10^{-3}kSG) \qquad (36)$$

F. Critical Compressibility (Z_c)

Critical compressibility may be conveniently calculated by the real gas equation-of-state at the critical point as follows:

$$Z_c = \frac{P_cV_cMW}{RT_c} = \frac{P_cV_cMW}{10.732\,T_c} \qquad (37)$$

G. Watson Factor (K)

The Watson factor is calculated from its definition as follows:

$$K = \frac{T_b^{1/3}}{SG} \qquad (38)$$

H. Acentric Factor (Edmister's Correlation) (ω)

$$\omega = \frac{3}{7}log\left[\frac{P_c}{14.696}\right] / \left[\left(\frac{T_c}{T_b}\right) - 1\right] - 1 \qquad (39)$$

J. Acentric Factor (Korsten's Correlation)

$$\omega = 0.5899log\left[\frac{P_c}{14.696}\right] / \left[\left(\frac{T_c}{T_b}\right)^{1.3} - 1\right] - 1 \qquad (40)$$

Where T_b and T_c are in °R, P_c is in psia, and V_c is in ft^3/lb.

4. Kesler-Lee Correlations

Kesler and Lee (1976) [12] developed a set of equations to evaluate properties of undefined petroleum fractions. Given specific gravity (SG) and boiling point (T_b) or molecular weight (Mw) of the petroleum fraction, physical properties are estimated as follows:

A. Molecular Weight (Mw)

$$Mw = -12{,}272.6 + 9{,}486.4SG + (8.3741 - 5.991SG)k + (1 - 0.77084SG - 0.02058SG^2)\left\{0.7465 - \frac{222.466}{k}\right\}\frac{10^7}{k} + (1 - 0.80882SG + 0.02226SG^2)\left\{0.3228 - \frac{17.335}{k}\right\}\frac{10^{12}}{k^3} \quad (41)$$

Where

$K = \frac{T_b}{1.8}$ (42)

B. Normal Boiling Point

In case boiling point (T_b) is not known and molecular weight (Mw) is given instead, the above equation is rearranged and solved iteratively for k. The objective function for the nonlinear solver is given by:

$$f(k) = -12{,}272.6 + 9{,}486.4SG + (8.3741 - 5.991SG)k + (1 - 0.77084SG - 0.02058SG^2)\left\{0.7465 - \frac{222.466}{k}\right\}\frac{10^7}{k} + (1 - 0.80882SG + 0.02226SG^2)\left\{0.3228 - \frac{17.335}{k}\right\}\frac{10^{12}}{k^3} - MW = 0 \quad (43)$$

C. Critical Temperature (T_c)

$$T_c = 1.8\left[189.8 + 450.6SG + (0.4244 + 0.1174SG)k + \frac{(0.1441 - 1.0069SG)10^5}{k}\right] \quad (44)$$

D. Critical Pressure (P_c)

$$P_c = 14.5038exp\left\{5.689 - \frac{0.0566}{SG} - \left(0.43639 + \frac{4.1216}{SG} + \frac{0.21343}{SG^2}\right)\frac{k}{10^3} + \left(0.47579 + \frac{1.182}{SG} + \frac{0.15302}{SG^2}\right)\frac{k^2}{10^6} - \left(2.4505 + \frac{9.9099}{SG^2}\right)\frac{k^3}{10^{10}}\right\} \quad (45)$$

D. Acentric Factor (ω)

$$\omega = \begin{cases} -7.904 + 0.1352k - 0.007465k^2 + 8.35T_{br} + \frac{(1.408 - 0.01063k)}{T_{br}} & T_{br > 0.8} \\ \frac{-ln\left(\frac{P_c}{14.696}\right) - 5.92714 + \frac{6.09648}{T_{br}} + 1.28862\ln(T_{br}) - 0.169347T_{br}^6}{15.2518 - \frac{15.6875}{T_{br}} - 13.4721\ln(T_{br}) + 0.43577T_{br}^6} & T_{br \leq 0.8} \end{cases} \quad (46)$$

where

$$T_{br} = \frac{T_b}{T_c} \quad (47)$$

$$K = \frac{T_b^k}{SG} \quad (48)$$

E. Critical Compressibility Factor (Z_c)

$$Z_c = 0.2905 - 0.0850\omega \quad (49)$$

F. Critical Volume (General Definition)

$$V_c = \frac{RT_cZ_c}{MWP_c} \qquad (50)$$

Where T_b and T_c are in °R, P_c is in psia, and V_c is in ft³/lb.

X. THERMOPHYSICAL PROPERTIES OF PETROLEUM FRACTIONS AND CRUDE OILS

1) API Gravity ($^\circ\boldsymbol{API}$): can be calculating by knowing oil specific gravity.

$$^\circ API = \frac{141.5}{SG\ @\ 60^\circ F} - 131.5 \qquad (51)$$

2) Correlation Index (CI): it can be calculated at TBP (50) as following:

$$C.I. = \frac{48640}{T_B} + 473.7SG - 456.8 \qquad (52)$$

3) Watson characterization factor (K) **[22],[2]**: by calculating volume average boiling point (VABP), K value can be estimated as following:

$$\text{VABP} = \frac{T_{10} + T_{30} + T_{50} + T_{70} + T_{90}}{5} \qquad (53)$$

Then, the mean average boiling point (MeABP) can be calculated after the calculation of Δ and SL as following:

$$\text{SL} = \frac{T_{90} - T_{10}}{90 - 10} \qquad (54)$$

$$ln\Delta = -\ 0.94402 - 0.00865(VABP - 32)^{0.6667} + 2.99791\ SL^{0.333} \qquad (55)$$

$$\text{MeABP} = \text{VABP} - \Delta \quad (56)$$

According to this value the crude oil can be classified as napthene base.

4) Pour Point: it is an index for paraffins an aromatic compounds.

$$\text{PP} = 753 + 136\left[1 - \exp\left(-0.15_{v_{100}}\right)\right] - 572SG + 0.0512_{v_{100}} + 0.139MeABP \qquad (57)$$

5) Cloud Point: can be estimated by knowing pour point from this equation:

$$logCP = -7.41 + 5.49logMeABP - 0.712MeABP^{0.315} - 0.133SG \qquad (58)$$

$$\text{PP} = 0.9895\ \text{CP} + 1.4 \quad (59)$$

6) Diesel Index: it is estimated by this relation:

$$Diesel\ Index = \frac{^\circ\text{API.Aniline point }(^\circ\text{F})}{100} \qquad (60)$$

XI. RESULTS AND DISCUSSION

Tobruk refinery is designed to process different petroleum crude oils including Messla and Sarir mix crude oils. The more important properties of this mix are listed in Table 1, while Table 2 shows the distillation products of crude oil. The true boiling point is varying for different fractions between initial boiling point (IBP) and the final boiling point (FBP). The true boiling point (TBP) of petroleum fractions according ASTM D86 method is reported in Table 3.

Table 1 : Properties of Messla and Sarir mix [3]

No.	Property	Value
1	API gravity @ 60 °F	38.9
2	Distillation test: IP 123/D86	
3	IBP, °C 670 mms	52.5
4	Final Boiling Point	365.0
5	Sulfur content, wt%	0.16
6	Kinematics viscosity @ 100 °F, cst	10.70
7	Salt content as NaCl, Ib/1000 bbl	3.2
8	Acidity, mg KOH/g	0.080
9	Hydrogen sulphide, ppm	< 1.0
10	Reid vapour pressure, kPa (psi)	6 (0.85)
11	Pour point, °C	24

Table 2 : Distillation products of crude oil [3]

Products	Light naphtha	Heavy naphtha	Kerosene	Diesel	Residue
True boiling point (TBP), °C	95	160	255	325	402
Distillation percent	15.4	31.5	22.9	18.8	11.02

Table 3 : True boiling points of petroleum fractions [3]

True boiling point (TBP), °C	Light naphtha	Heavy naphtha	Kerosene	Diesel
IBP	32	79	112	200
5% vol.	53	137	166	211
10% vol.	63	138	169	221
20% vol.	68	141	171	232
30% vol.	75	142	175	242
40% vol.	81	144	176	252
50% vol.	87	146	179	264
60% vol.	95	148	180	278
70% vol.	102	149	183	291
80% vol.	108	152	185	307
90% vol.	116	155	189	326
95% vol.	121	158	192	340
FBP	132	172	202	347

XII. CALCULATIONS OF PHYSICAL PROPERTIES OF PETROLEUM FRACTIONS

The calculations of physical properties of petroleum fractions are reported in Table 4 by correlations models using the equations (1) through (50). The petroleum fractions are light naphtha, heavy naphtha, kerosene and diesel. These properties include critical temperature (T_c), critical pressure (P_c), critical volume (V_c), acentric factor (ω) , Watson factor (K), compressibility factor (Z_c) and molecular weight (Mw).

The different parameters of calculations for the petroleum fractions (Light naphtha, Heavy naphtha, Kerosene, Diesel) were compared with other published data e.g. Cavett, Twu, Riazi-Daubert and Kesler-Lee. The obtained results show more or less similarity between the applied correlations for the calculated physical properties of different petroleum fractions (Table 4). However, Figures 1 through 7 depict these similarities.

XIII. THERMOPHYSICAL PROPERTIES OF PETROLEUM FRACTIONS AND CRUDE OILS

The calculation of some thermophysical properties of petroleum fractions and crude oils by using the equations (51) (API Gravity, Correlation Index, Watson characterization factor, Pour Point, Cloud Point, Diesel Index) through (60) are reported in Table 5. The obtained results within the characterization features of required products.

Table 4 : Calculated physical properties

Correlations	Light naphtha	Heavy naphtha	Kerosene	Diesel
Critical temperature (T_c)				
Cavett	511.2	540.0	710.2	780.0
Twu	520.9	556.3	705.6	783.5
Riazi-Daubert	504.5	580.8	704.9	790.2
Kesler-Lee	502.2	580.4	701.2	786.3
Critical pressure (P_c)				
Cavett	32.0	25.9	17.2	12.8
Twu	35.2	24.9	16.9	13.0
Riazi-Daubert	34.1	26.2	17.5	13.4
Kesler-Lee	33.4	26.8	17.9	12.7
Critical volume (V_c)				
Cavett	380.2	505.1	830.2	1203.0
Twu	375.5	498.2	835.6	1199.6
Riazi-Daubert	390.5	500.1	822.0	1220.0
Kesler-Lee	370.2	488.5	850.4	1175.7
Acentric factor (ω)				
Cavett	0.3751	0.4233	0.4351	0.5899
Twu	0.4222	0.4031	0.4424	0.5911
Riazi-Daubert	0.3850	0.4199	0.4569	0.6036
Kesler-Lee	0.4211	0.4422	0.4980	0.5966
Watson factor (K)				
Cavett	11.8021	11.8212	11.7812	11.8900
Twu	11.5914	11.8421	11.8811	11.9011
Riazi-Daubert	11.8125	11.8311	11.7588	11.8920
Kesler-Lee	11.7721	11.8400	11.7844	11.9020
Compressibility factor (Z_c)				
Cavett	0.2450	0.2477	0.2378	0.2455
Twu	0.2488	0.2461	0.2422	0.2399
Riazi-Daubert	0.2499	0.2457	0.2366	0.2324
Kesler-Lee	0.2410	0.2441	0.2315	0.2311
Molecular weight (Mw)				
Cavett	146	152	165	173
Twu	144	154	172	171
Riazi-Daubert	147	153	162	170
Kesler-Lee	145	155	171	173

Table 5 : Thermophysical properties of petroleum fractions and crude oils

°API Gravity	Correlation Index (CI)	Watson characterization factor (K)	Pour Point	Cloud point	Diesel index
38.5	6.03	11.45	22.84	21.66	51

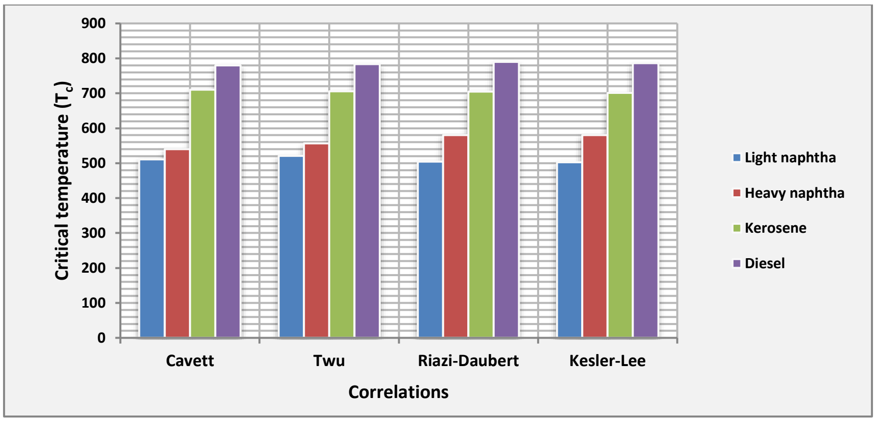


Fig. 3: Critical temperature of petroleum fractions

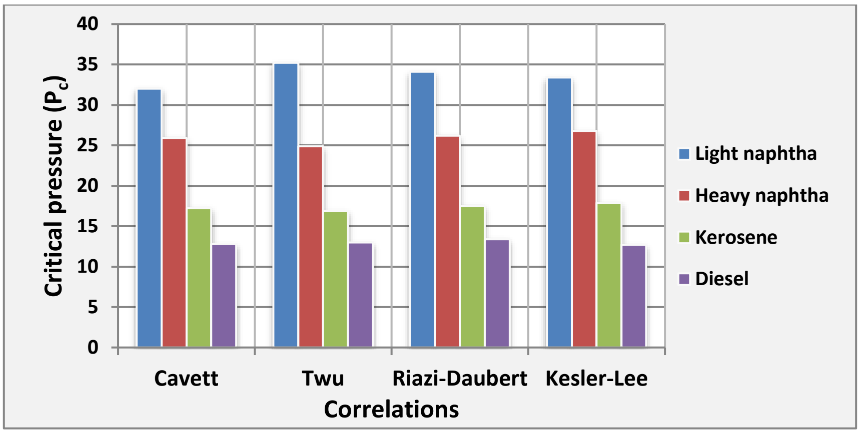


Fig. 4: Critical pressure of petroleum fractions

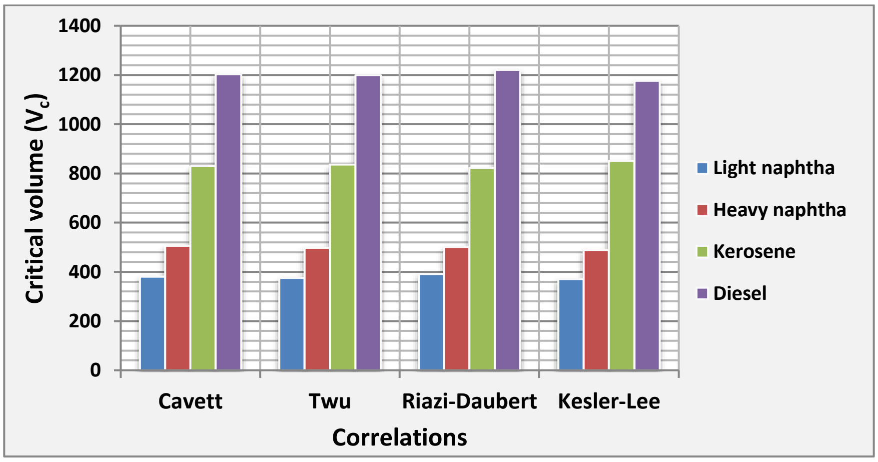


Fig. 5: Critical volume of petroleum fractions

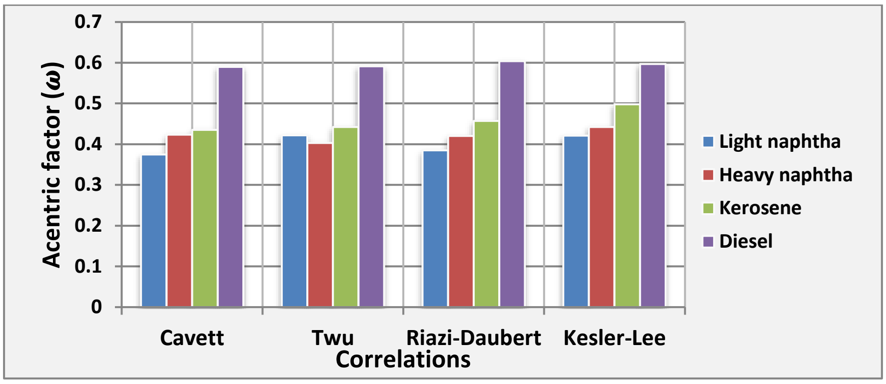


Fig. 6: Acentric factor of petroleum fractions

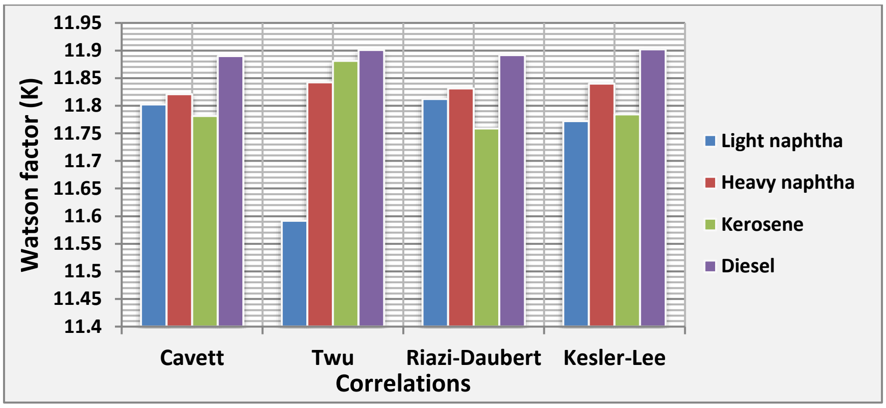


Fig. 7: Watson factor of petroleum fractions

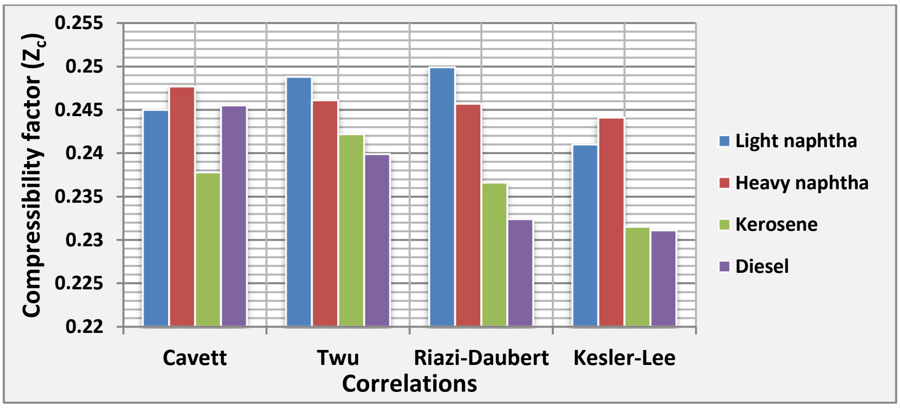


Fig. 8: Compressibility factor of petroleum fractions

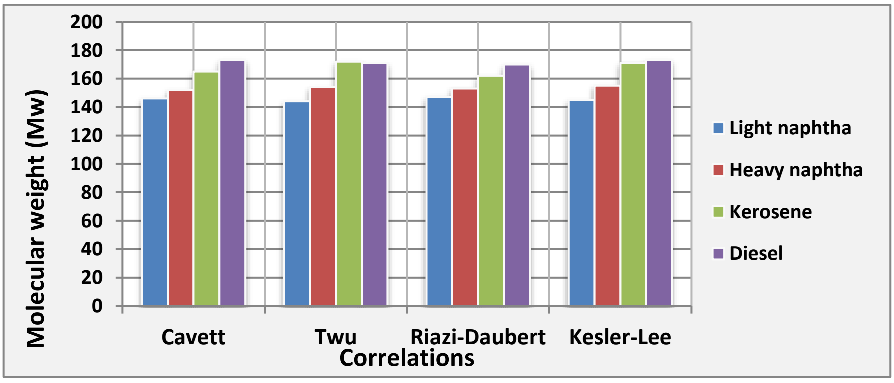


Fig. 9: Molecular weight of petroleum fractions

XIV. CONCLUSION

The most common correlations for characterizing undefined petroleum fractions, that were presented in literature and have gotten a wide acceptance in the oil industry, are revised. The only required input parameters are specific gravity and normal boiling point or molecular weight. Calculated properties include: normal boiling point (if molecular weight is supplied), molecular weight (if normal boiling point is supplied), critical properties and acentric factor.

Empirical correlations were extensively used in calculating PVT properties. Estimation of the missing quantities: γ, Mw and Tb. The specific gravity γ, the molecular weight M, and the normal boiling point Tb form the minimum set required for the characterization of a narrow petroleum fraction. Sometimes, experimental values of two of them (typically Tb and γ, or M and γ), are unknown and have to be estimated. TBP data for oils from a similar region can be used as a good reference.

In this study, the known physical properties including γ and Tb are generally used in correlation models to estimate the properties of petroleum fractions of crude oils under considerations. The calculations reveal that there is no much difference between correlation models and the obtained results seem to be very close with similar published data. These correlations can be applicable to predict the physical properties of petroleum fractions of different crude oils.

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