

Improved Characterization of Heptane Plus Fraction of Niger Delta Light Crudes

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ABSTRACT

Accurate determination of molecular weight of heptane plus (C_{7+}) fractions is essential in reliable phase behavior calculations and compositional EOS modeling studies. Empirical correlations provide cheaper alternatives in time and cost, to obtaining reliable molecular weight data than by experiments, though with compromised accuracies.

Several empirical correlations developed to predict molecular weight of C_{7+} fractions of petroleum were reviewed. A new correlation for calculating molecular weight of heptane plus fractions of light crudes was developed from a database compiled from Niger Delta fields for over 1,200 light crude oil assays, conventional PVT reports, and literature data. The correlation was developed using rational multiple regression analysis method.

The new correlation's performance was compared with five others which do not depend on boiling point temperatures. Results showed that the new correlation has superior performance with the lowest absolute average and relative mean square errors. The new correlation had an average relative error of 8.15%, root mean square error of 0.09% and correlation coefficient of 0.955.

Keywords-- Specific Gravity, API Gravity, PVT Properties, Molecular Weight, Condensate, Heptane Plus Fractions, Niger Delta Crude Oils

I. INTRODUCTION

Crude oil systems from various oil-producing regions of the world exhibit regional trends in chemical composition, placing them into one of three groups: paraffinic, naphthenic and aromatic, based on the type of C-C bonding which characterize the molecules. Paraffin hydrocarbons are characterized by open or straight chains joined by single bonds. Isomers of straight chain

compounds containing branched chains are a part of this group; Naphthene hydrocarbons are saturated (single bonded) carbon molecules that exist as ringed molecules called cycloparaffins. Aromatic hydrocarbons are also cyclic but differ from Naphthenic hydrocarbons in having alternating single and double bonds (benzene derivatives).

Crude oils tend to be a complex mixture of paraffins, naphthenes and aromatics. Crude oil mixtures which have predominance of paraffin hydrocarbons are called paraffin-based or paraffinic crudes. This group are the most stable and most predominant of all. Crude oils containing a large percentage of cycloparaffins in the heavy components are categorized as Naphthenic based crudes. These make up the second primary constituent of crude oil. Highly aromatic crudes are less common but are still found around the world (Pirson, (1977)).

Condensates and light crudes consist largely of hydrocarbons from C_1 to C_6 , some non-hydrocarbon compounds such as sulfur, nitrogen and carbon dioxide, as well as undefined compounds ranging from C_7 to heavier hydrocarbon groups collectively called heptane plus fractions or C_{7+} . A proper description of the physical properties of the plus fractions is essential in performing reliable phase behavior calculations and compositional modeling studies. Molecular weight variation is a reliable means of characterizing oil types on the basis of their chemical differences.

Knowledge of molecular weight of condensates and heptane plus fractions serve as necessary data in the determination of relevant petroleum engineering parameters such as gas equivalence of oil and well-stream specific gravity, defined below, to mention but a few.

Gas Equivalence of Oil: In converting stock tank barrels of condensates to gas volumes in SCF, knowledge of M_o is required for the computation as follows:

$$GE_{oil} = 133\,000 \gamma_o / M_o$$

Where,

γ_o = oil relative density, and

M_o = molecular weight of condensate or oil.

(1)

GE_{oil} = gas equivalence of oil (SCF/STBO);

Well-stream Specific Gravity: Gas mixtures that produce condensate at surface conditions may exist as a

single phase gas in the reservoir and production tubing such as in wet gas or gas condensate reservoir fluids. If well

stream properties are desired at conditions where the mixture is single-phase, surface-gas and oil properties are γ_w calculated as follows:

$$\gamma_w = \frac{\bar{\gamma}_g + 4,580R_p\gamma_o}{1 + 133,000R_p(\gamma_o/M_o)} \tag{2}$$

Where, γ_w = gravity,

relative density of oil

The relative density of oil is defined as

$$\gamma_o = \frac{\rho_o}{\rho_w} \tag{3}$$

Where, γ_o = gravity,

The density of petroleum oils is expressed in the United States in terms of American Petroleum Institute (or API) gravity rather than specific gravity.

$$^{\circ}API = \frac{141.5}{\gamma_o} - 131.5 \tag{4}$$

Using degree API, oil relative gravity is defined as:

$$\gamma_o = \frac{141.5}{(^{\circ}API + 11.5)} \tag{5}$$

Where,

γ_o is the specific gravity of the crude oil at 60 °F, (water = 1).

The API gravity scale acts as an inverse relationship to density (and specific gravity), that is, as density increases, the API gravity decreases. Therefore,

used to convert to a well-stream specific gravity,

M_o = surface condensate molecular weight and γ_o =

R_p = producing oil (condensate)/gas ratio;

$\bar{\gamma}_g$ = average surface-gas

ρ_o = oil density; and ρ_w = water density at standard conditions (62.4lb m/ft³).

crude oil samples can be graded by their API gravity as shown by table 1.

Table 1. Classification of crudes based on $^{\circ}API$

$^{\circ}API$	Crude oil category
$> 31.5^{\circ}$	Light Crude Oil
$22.1^{\circ} \leq ^{\circ}API \leq 31.5^{\circ}$	Intermediate Crude Oil
$^{\circ}API < 22.1^{\circ}$	Heavy Crude Oil

Reliable data on molecular weight of condensate oil samples and heptane plus fractions of light crudes are best obtained from experimental techniques. The true boiling point (TBP) distillation technique provides the key data for heptane plus characterization, including mass and molar quantities, specific gravity, molecular weight, and boiling point of each distillation cut. However, experimental methods are costly in time and monetary terms. Use of correlations provides cheaper alternatives to obtaining data with applaud-able success. However, due to compositional differences, correlations developed from regional samples, predominantly of one chemical base, may

not provide satisfactory results when applied to crude oils from other regions.

II. REVIEW OF LITERATURE

2.1 Watson's(1933) Characterization factor, K_w , also referred to as Watson's K factor, was introduced in 1933 by Watson and Nelson as a correlative factor to be used in classifying crude oils as paraffinic, naphthenic or aromatic. They defined K_w as a ratio between the mean average boiling point and specific gravity as follows:

$$K_w = \frac{T_b^{(1/3)}}{\gamma_o} \tag{6}$$

where:

K_w = Watson's K factor,

boiling point in R (degree Rankine) and

Depending on the value of the Watson characterization factor, crude oils are classified as paraffinic

T_b = Mean average normal

γ_o = specific gravity of oil at 60°F

($K_w = 11-12.9$), naphthenic ($K_w = 10-11$), or aromatic ($K_w < 10$). The range for whole crudes is 10.5 to 12.9.

The Watson factor and the boiling point are related together through the API gravity. Bergman & Sutton (2007) presented a plot of Watson factor versus crude oil API gravity from a database compiled from all over the

$$K_w = 11.2 + 0.0192164 API$$

Naji (2011) plotted average boiling point (T_b) versus (API) for both pure components and crude oils. The plot, shown as figure 1 below, shows that the T_b curves, for pure components and crude oils, tend to converge for API gravities higher than 30. On the other side, for API gravities lower than 30; *i.e.* for heavy fractions, the T_b curve for pure

world for over 3000 crude oil assays, conventional PVT reports, and literature data. For simulation purposes, the linear fitting for the plot is:

$$(7)$$

components gets higher than the T_b curve for crude oils as API gravities decrease. This suggests that T_b equation for pure components may be suitable for crude oils having API gravities higher than 30.

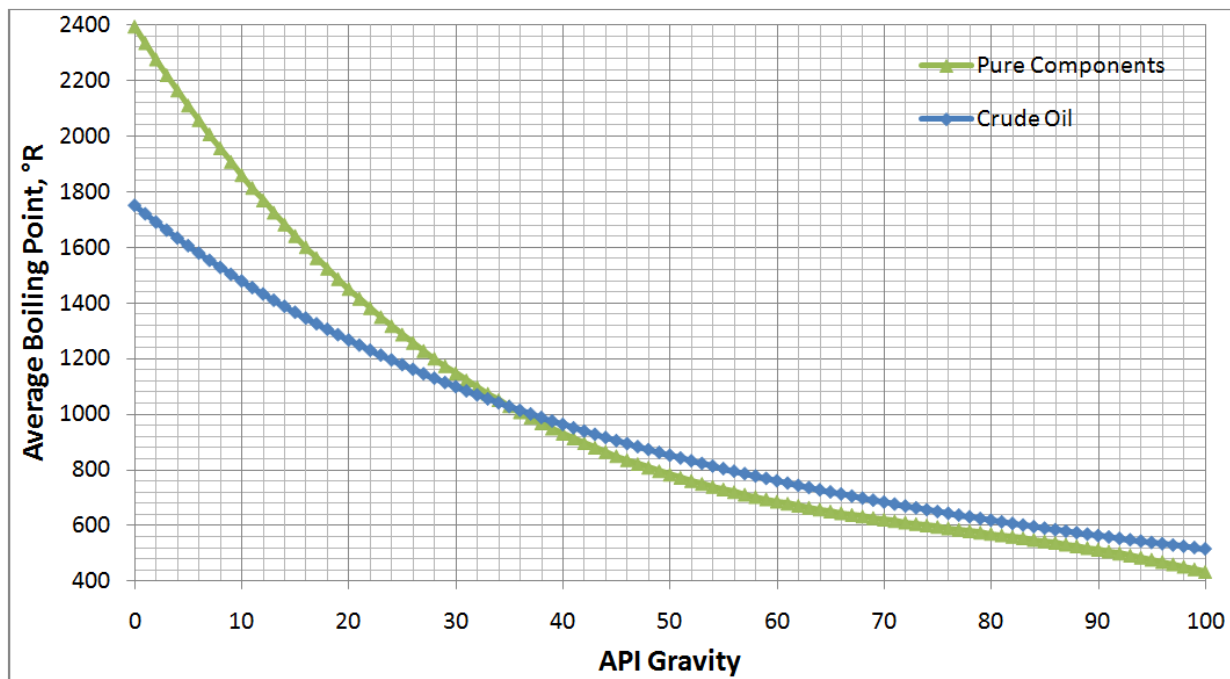


Figure 1. Plot of average boiling point versus API gravity for pure components and crude oils

Based on the relationship between boiling point temperature and API gravity of Figure 1 Naji (2011),

$$T_b = 1748 - 30.05API + 0.3451API^2 - 0.002416API^3 + 7.397 \times 10^{-6}API^4 \tag{8}$$

2.2 Compositional Mixing Using Kay (1936) mixing rule: Molecular weight of crude oil samples can be determined easily where the mole fractions of all

suggested the mathematical relationship between T_b and API to be as follows:

constituents are known by use of Kay (1936) mixing rule as follows:

For a mixture having ' N ' components, the molecular weight is

$$M_o = \sum_{i=1}^N z_i M_i,$$

Where,

M_o = Apparent Molecular weight of mixture,

M_i = molecular weight of pure component i in mixture;

z_i = mole fractions of components in the mixture; and the sum of z_i for $i = 1, 2, 3, \dots, N$ is 1.0.

(By convention, oil composition is denoted by x_i and gas composition by y_i).

N = number of constituents of mixture;

2.3 Molecular Weight Correlations: There are various mathematical correlations that have been developed to

predict the molecular weights of condensates and heptane plus fractions. Most of these correlations are based on the

basic properties of average boiling points and specific gravities. Molecular weight of crude oil and oil fractions are affected by oil composition (specific gravity and characterization factor), boiling point temperature and system pressure. Some of the popular correlations are:

Cragoe’s correlation is

$$M = \frac{6084}{\gamma_{API} - 5.9} \tag{10}$$

2.3.2 Standing’s (1947) Correlation: Standing’s correlation for estimating the molecular weight of oil was based on

$$M = 240 - 2.22\gamma_{API} \tag{11}$$

Where, M is effective molecular weight of tank oil and

γ_{API} is $^{\circ}API$.

2.3.3 Eilert’s (1947) Correlation: Eilert’s correlation is credited to be reliable for most condensates. and has the form:

$$M = \gamma_o \left((1.892 * 10^{-3}) + (7.35 * 10^{-5})\gamma_{API} - (4.52 * 10^{-8})\gamma_{API}^2 \right)^{-1} \tag{12}$$

2.3.4 Lasater’s (1958) Correlation: Lasaterin 1958 presented a mathematical correlation for estimating

$$M = \left(\frac{K_w \gamma_o^{0.84573}}{4.5579} \right)^{6.58848} \tag{13}$$

Where,

K_w for Niger delta crudes = 11.7(28)

2.3.5 Kesler and Lee (1976) Correlation: Kesler and Lee in 1976, proposed a correlation for prediction of molecular weight on the basis of regression analysis of hydrocarbon

$$M = -12272.6 + 9486.4\gamma_o + (8.3741 - 5.9917\gamma_o)T_b + (1 - 0.77084\gamma_o - 0.02058\gamma_o^2) * (0.7465 - 222.466/T_b) 10^7/T_b + (1 - 0.80882\gamma_o + 0.02226\gamma_o^2) * (0.32228 - 17.335/T_b) 10^{12}/T_b^3 \tag{14a}$$

Where,

$$T_b = K_w x 1.8 \tag{14b}$$

2.3.6 Sim and Daubert (1980) Correlation: Sim and Daubert developed an analytical relationship in 1980 that used specific gravity and boiling point as the correlating

$$M_o = 1.4350476 * 10^{-5} T_b^{2.3776} \gamma_o^{-0.9371} \tag{15}$$

2.3.7 Riazi and Daubert (1987) Correlation: Riazi and Daubert in 1987 developed a simple two-parameter equation for predicting the physical properties of pure compounds

$$\theta = a\theta_1^b \theta_2^c \tag{16a}$$

where, θ is the property to be predicted, θ_1 and θ_2 are any two input parameters that should represent molecular energy and molecular size. This input parameters pair (θ_1 ,

2.3.1 Cragoe’s (1929) Correlation: Cragoe’s correlation is popular in the oil industry for use in estimating molecular weight of condensates and heptane plus fractions.

reservoir fluid data systems from California, USA, and has the form:

effective molecular weight of stock tank oil as a function of oil specific gravity, γ_o and K_w as follows:

K_w = Watson’s K factor

data within molecular range of 60 to 650. The relationship expresses molecular weight as function of specific gravity and boiling point as follows:

parameters for calculating the molecular weight of the undefined petroleum fraction as follows:

and undefined hydrocarbon mixtures. Their mathematical expression has the following form

θ_2) can be (T_b, γ), (T_b, I), (T_b, CH), (M, γ), (M, I), (M, CH), (μ, γ), (μ, I), or (μ, CH).

T_b is normal boiling point, in Kelvin.

I is the refractive index parameter at 20 °C.

M is molecular weight.

CH is Carbon to Hydrogen weight ratio.

γ is the specific gravity at 15.5 °C, and

μ is the kinematic viscosity at 38 °C.

The constants a , b , and c are based on the properties of hydrocarbons with carbon number range C_5 to C_{20} . This range is equivalent to the molecular weight range of 70-300, and the boiling point range from 300 to 616 K (26 to 343.33 °C). By using this equation, properties such as

$$M = aT_b^b \gamma_{API}^c \tag{16a}$$

Where,

M is molecular weight, crude oil or oil fraction, plus fraction, and

a, b and c are correlation constants which determine the accuracy of resultant correlation.

The regression constants a, b and c have the values, 1.6607×10^{-4} , 2.1962 and -1.0164 , respectively,

$$M = 1.6607 \times 10^{-4} T_b^{2.1962} \gamma_{API}^{-1.0164} \tag{16c}$$

The equation is valid for the hydrocarbons with molecular weight range from 70 to 700, and boiling point range from 300 to 850 K (32 to 566 ° C), which is equivalent to the API range from 14.4 to 93.1

$$\theta = a \text{EXP}(b \theta_1 + c \theta_2 + d \theta_1 \theta_2) \theta_1^e \theta_2^f \tag{17a}$$

The correlation constants a to f have the values as follows: $a = 42.965$, $b = 2.097 \times 10^{-4}$, $c = -7.78712$, $d = 2.08476 \times 10^{-3}$, $e = 1.26007$ and $f = 4.98308$.

$$M = 42.965 \text{EXP}[2.097 \times 10^{-4} T_b - 7.78712 \gamma_o + 2.08476 \times 10^{-3} T_b \gamma_o] T_b^{1.26007} \gamma_o^{4.98308} \tag{17b}$$

2.3.9 Pedersen et al (1989) Correlation: Pedersen, Fredeslund and Thomassen in 1989, presented a correlation for calculating molecular weight of oil fractions as follows:

$$M = 42.965 [\text{exp}(2.097 \times 10^{-4} T_b - 7.78712 \gamma_o + 2.08476 \times 10^{-3} T_b \gamma_o)] T_b^{1.26007} \gamma_o^{4.98308} \tag{18}$$

2.3.10 Da Silva and Rodriguez (1992) Correlation: DaSilva and Rodriguez proposed a correlation for determining the molecular weight in 1992 with the following formula:

$$M_o = 64.2576 \text{EXP} \left[\frac{T_b - 460}{447.08723} \right] \tag{19}$$

2.3.11 Isehunwa and Falade (2007) Correlation: Isehunwa and Falade in 2007 used Nigeria's Niger Delta regional data to obtain two correlations for crude oil and

$$M_o = 9260.1 (\gamma_{API})^{-1.2894} \tag{20a}$$

And for molecular weight of heptane plus fractions has the form:

$$M_{C_7+} = 459.75 - 16.67 \gamma_{API} + 0.1778 \gamma_{API}^2 \tag{20b}$$

The review of literature revealed that the correlations developed with data from Niger delta for characterizing Niger delta crudes based on molecular weight of heptane plus fractions are inadequate in number and in accuracy. In fact, only the correlation of Isehunwa

density at 20°C, molecular weight, critical properties, refractive index, and heat of vaporization can be predicted successfully.

For molecular weight determination, the Riazi and Daubert (1987) Correlation has the form:

T_b is the normal boiling point of γ_{API} is API gravity of reservoir crude oil or oil heptane

so that the Riazi and Daubert's correlation for molecular weight with the correlation parameters has the form:

2.3.8 Modified Riazi-Daubert (1987) Correlation: In order to improve on accuracy and range of applicability, Riazi and Aubert modified their earlier correlation in 1987 to a generalized form of:

By substituting the regression constants into Eq. (17a), the molecular weight correlation has the form as shown by Eq. (17b)

heptane plus molecular weights, respectively. Their correlation for stock tank oil molecular weight has the following form:

and Falade (2007), was found to be based on Niger Delta crudes from the literature. This study aims to provide an alternative means of characterizing heptane plus fractions with improved accuracy for use with data from Niger delta. It also aims to explore the possibility of finding a

correlation based on other geographic origins for use in characterizing Niger Delta crudes with minimal errors.

III. METHODOLOGY

Research methodology involved first collecting data for Niger Delta crudes available in published literature. The next step was to develop multiple regression models and attempt to reproduce data collected with goal of finding a best fit model with minimal bias between experimental values and estimated values. The performance of the correlation established as best fit is compared to the

$$M = a\gamma_{API}^c$$

Where, *a* and *c* are regression parameters.

Using multiple rational regression technique to connect the independent variable, (*M*) to the independent variable, (γ_{API}), optimum values of the regression parameters *a* and *c* which gave minimal error of estimation of molecular weight of heptane plus fractions for Niger

$$Objective\ function = |RMSE|_{min} = \left[\frac{1}{N} \left(\sum_{i=1}^N \left(\frac{X_i^{est} - X_i^{exp}}{X_i^{exp}} \right)^2 \right) \right]^{1/2} \tag{23}$$

The resultant relation which satisfied the objective of minimization of RMSE for M_{C_7+} estimation has the

$$M_{C_7+} = 7700\gamma_{API}^{(-1.25)} \tag{24}$$

3.2 Ranges of crude oil properties and composition of samples used for the study

More than 1,286 data from five reservoirs obtained from literature were used in the model development in this

performances of popular industry models. Statistical error analysis is used to evaluate performance.

3.1 Model Development

Model development objectives were to determine a simple correlation, easy to memorize that would satisfy the requirement of improved accuracy in estimating the molecular weight of heptane plus fractions of Niger delta light crudes. For simplicity, the generalized form of Riazi and Daubert (1987) Correlation, Eq.(16b) was adopted as a starting point for this study.

By assuming that the contribution due to boiling temperature is assumed insignificant, such that the regressing parameter, *b*=0, the resulting equation becomes:

delta crudes were determined. The optimal values were determined by seeking the values which minimized Relative Mean Square Error (RMSE) when estimated values were compared against experimental values obtained from literature (10). That is, objective function is given as:

parameters, *a* and *c* as 7700 and 1.26, respectively, so that the new correlation has the form below:

study. The ranges of crude oil properties and composition of samples used for the study are as listed in Table 2.

Table 2. PVT Property Ranges of Crude Oil Mixtures used for this study

Laboratory Measured Parameters	Minimum	Maximum
Oil gravity, ($^{\circ}API$)	15.99	54.68
Under-saturated oil viscosity, $\mu_o(cp)$	0.11	104.3
Specific gravity of surface oil	0.756	0.818
Saturation pressure (<i>psia</i>)	240	5105
Bubble point oil FVF, $B_{ob}(bbl/STB)$	1.047	4.474
Mean Composition of Crude Oil and Condensate Samples		
H_2S	0.00	0.816
N_2	0.08	3.38
CO_2	0.001	4.44
C_1	57.38	84.15
C_2	2.26	8.22
C_3	1.15	4.19
<i>i</i> C_4	0.24	2.05
<i>n</i> C_4	0.3	1.70
<i>i</i> C_5	0.16	1.16

$n C_5$	0.13	0.61
C_6	0.22	0.90
C_{7+}	1.30	3.03

IV. RESULTS AND DISCUSSION

The performances of the new correlation and ten others, reviewed in this study, in reproducing experimentally obtained values were statistically analyzed. The statistical parameters that were used in this study to measure each method's performance are absolute relative percentage error (ARE), percentage absolute average

relative deviation, (AARD), maximum relative error, ($E_{i_{max}}$), minimum relative error, ($E_{i_{min}}$), Root mean squared error, (RMSE) and correlation coefficient or R^2 . The formulae for these statistical tools are contained in the Appendix and the results of the analyses of errors are summarized in Table 3 below.

Table 3 Statistical Accuracy of Molecular Weight Correlations

Correlation	$E_{i_{min}}$	$E_{i_{max}}$	ARD, %	AARD, %	RMSE	R^2
This Study	0.001	0.534	8.15	8.15	0.09	0.955
Isehunwa and Falade	0.097	0.643	13.55	13.55	0.26	0.952
Standing	0.139	2.399	125.13	125.13	1.05	0.847
Da Silva & Rodriguez	0.001	1.475	14.35	14.35	0.55	0.825
Sim & Daubert	0.070	1.361	-11.41	11.41	0.72	0.805
Lasater	0.274	2.101	78.87	78.87	1.35	0.723
Eilert	0.0845	2.770	117.05	117.05	1.35	0.771
Cragoe	0.4547	2.670	154.23	154.23	1.65	0.633
Modified Riazi & Daubert	0.198	14.249	396.71	396.71	6.02	0.192
Kesler & Lee	0.032	1735.1	-5718.22	5718.22	1659.28	-9.62E (-05)
Riazi & Daubert	0.6414	0.994	-85.47	85.47	0.89	-12.52

The results show that the new correlation has the lowest parentage average absolute deviation error of 8.15 which is the only correlation with AARD less than 10. This

is a significant contribution of this study. This information is best appreciated by the comparative plot of AARD for the correlations studied shown as figure 2 below.

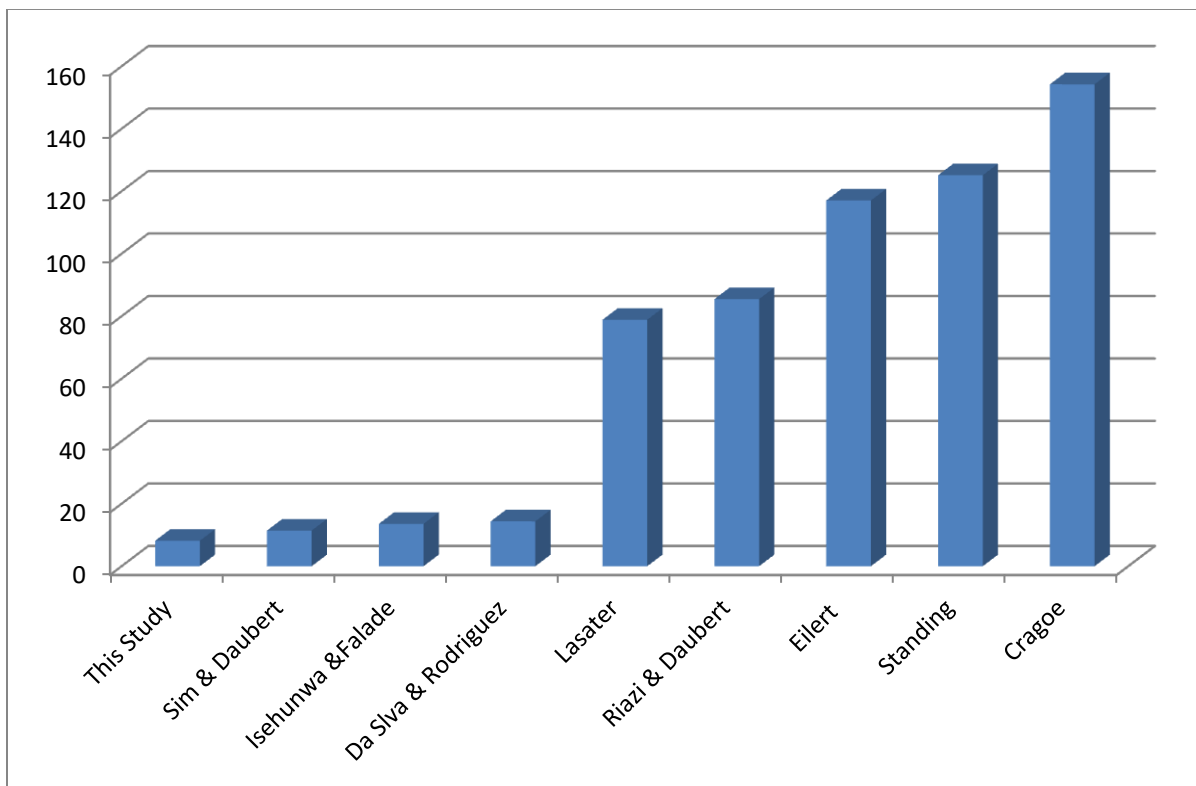


Figure 2. Comparative AARD, % for Molecular Weight Correlations

The root mean square error of the new correlation is lower than for all the other correlations having a value of 0.09. This implies that the new correlation better captures molecular weights of heptane plus fractions calculated with smaller variations between the negative and positive errors of estimation.

The new correlation had the smallest minimum and smallest maximum absolute relative errors (0.001 and 0.534, respectively). This shows that there is good agreement between the estimated and experimental data with a smaller degree of scatter when using the new correlation.

The correlation coefficient for the new correlation is 0.955. This is the highest value obtained from all the correlations reviewed in this study. This signifies that the new correlation has a better positive agreement between the estimated values and the independent variable, making the new correlation a better estimator of molecular weight of C_7^+ fractions for Niger Delta light crudes than the other correlations to which it was compared.

The correlation coefficient for calculated for the Riazi and Daubert correlation is very low (0.192), implying that there is hardly any correlation between the estimator or independent parameter and the values being estimated or the independent parameters, for Niger delta crudes.

Kesler and Lee’s correlation as well as Riazi and Daubert’s correlation give negative correlation coefficients suggesting a negative correlation between molecular weight and specific or API gravity for Niger delta crude oils. This is completely unacceptable, but understandable, considering that these correlations were not developed using Niger Delta regional data. This reason is true for all the correlations reviewed in this study except the correlation of Isehunwa and Falade.

The AARD (%) of modified Riazi and Daubert and Kesler and Lee’s correlations were not included in figure 2 above because of their extreme high values (396.71 and 5718.22, respectively) dwarf all others and diminish the significance of this evaluation method.

Though the correlation of Sim and Daubert’s has a lower AARD than the Isehunwa and Falade correlation which was based on Niger Delta data, it has a higher relative mean square error (RMSE = 0.72) against Isehunwa and Falade’s RMSE of 0.26. Also, the correlation of Isehunwa and Falade has a correlation coefficient of 0.952 which is higher than that of Sim and Daubert’s at 0.805. Thus, the Isehunwa and Falade’s correlation would perform better than the Sim and Daubert’s correlation when used with Niger Delta crude oil samples.

Table 4 presents the summary of the actual performances of the new correlation and next three best correlations based on correlation coefficients only. Data

used for case study is based on experimental data of Niger Delta crude oil samples obtained from literature(9). That is,

only the best four correlations, based on results of R^2 of Table 3 are included in Table 4 below.

Table 4. Comparison of New Correlation and 3 others for estimating molecular weight of heptane plus fractions of Niger Delta light crude oils

API Gravity	M_{C_7+} (Exp)	M_{C_7+} (Standing)	M_{C_7+} (Da Silva & Rodriguez)	M_{C_7+} (Isehunwa & Falade)	M_{C_7+} (This Study)
22.30	159.08	189.93	246.24	169.04	158.89
23.99	231.20	186.21	217.18	153.85	145.03
45.38	50.60	139.18	36.37	67.66	65.37
45.38	63.80	139.18	36.37	67.66	65.37
45.38	46.33	139.18	36.37	67.66	65.37
19.03	229.79	197.13	312.41	207.42	193.73
36.95	79.60	157.70	77.25	88.17	84.52
19.03	126.25	197.13	312.25	207.42	193.73
17.45	193.04	200.62	349.74	232.02	215.90
38.98	73.71	153.24	64.85	82.79	79.06
41.06	83.98	148.67	53.98	76.96	74.08
41.06	68.07	148.67	53.98	76.96	74.08
41.06	74.96	148.67	53.98	76.96	74.08
45.38	53.30	139.18	36.37	67.66	65.37
20.65	181.06	193.57	277.88	186.70	174.92
34.97	95.68	162.06	91.28	94.66	90.55
23.99	148.68	186.21	217.18	153.85	145.03
34.97	91.34	162.06	91.28	94.66	90.55
36.95	96.45	157.70	77.25	88.17	84.52
45.38	54.01	139.18	36.37	67.66	65.37
22.30	120.67	189.93	246.24	169.04	158.89
20.65	150.70	193.57	277.88	186.70	174.92
19.03	178.82	197.13	312.41	207.42	193.73
22.30	161.70	189.93	246.24	169.04	158.89
22.30	130.50	189.93	246.24	169.04	158.89
31.14	139.10	170.48	124.86	109.92	104.67
54.68	34.90	116.69	14.52	53.19	51.79
38.98	84.60	153.24	64.85	82.29	79.06
45.38	50.33	139.18	36.37	67.66	65.37

V. CONCLUSIONS

The conclusions from this study are:

- A new correlation which improves estimation of molecular weights of heptane plus fractions of Niger Delta crude oils has been developed.
- The new correlation is simple, having only one independent variable and two regressing parameters, only one of which is a non-integer.
- The new correlation was compared with ten other correlations of popular industry use, one of which was based on Niger Delta data for its development. The new correlation gave lowest value of average absolute relative deviation (AARD = 8.15) and

relative mean square errors (RMSE = 0.09), with the highest value of correlation coefficient of 0.955 indicating that it is a better estimator of molecular weights of undefined petroleum fractions of Niger Delta crude samples than the other correlations to which it was compared.

- The correlation coefficient is not sufficiently close to 1, being less than 1 by more than 4% which suggests room for improvement.
- The next best correlation when predicting molecular weights of undefined petroleum fractions of Niger Delta crude samples, after that presented in this study, is that of Isehunwa and Falade.

- Correlations not based on Niger Delta data but which could be used in predicting molecular weight of heptane plus fractions of Niger Delta crude oil samples, if accuracy were not so critical, are Standing's, Da Silva and Rodriguez's and Sim and Daubert's correlations.

REFERENCES

- [1] Almarray, J. A. (1983). *Prediction of liquid recovery from a gas condensate reservoir*. Doctoral Dissertation, Petroleum Engineering Department, COMER, WVU.
- [2] Bergman, D.F. & Sutton, R.P. (2007). *A consistent and accurate dead-oil-viscosity method*. Paper SPE-110194, SPE Annual Technical Conference and Exhibition, Anaheim, California, USA.
- [3] Pakistan. (1986). *Core laboratory report of Dhakni gas condensate field for oil and gas development corporation*. Available at: <https://www.osti.gov/servlets/purl/5723504>.
- [4] Craft, B. C. Hawkins, M., & Terry, R. E. (1991). *Applied petroleum reservoir engineering*. (2nd ed.). Englewood Cliffs. New jersey: Prentice Hall Inc..
- [5] Cragoe, C. S. (1929). *Thermodynamic properties of petroleum products*. U. S. Dept. of Commerce, Washington, DC: Miscellaneous Publications, pp. 97.
- [6] Da Silva, M. B. & Rodriguez, F. (1992). *Automatic fitting of equations of state for phase behavior matching, society of petroleum engineers*. SPE Latin America, Petroleum Engineering Conference, Caracas, Venezuela.
- [7] Eilerts, C. K. (1947). *Gas condensate reservoir engineering, 1. The reservoir fluid, its composition and phase behavior*. Available at: <https://www.osti.gov/biblio/5399737-gas-condensate-reservoir-engineering-reservoir-fluid-its-composition-phase-behavior>.
- [8] Firoozabadi, A., Hekim, Y., & Katz, D. (1978). *Reservoir depletion calculation for gas condensate using extended analysis in PR-EOS*. Available at: <https://onlinelibrary.wiley.com/doi/abs/10.1002/cjce.5450560515>.
- [9] Isehunwa, O. S. & Falade, G. K. (2007). *Improved characterization of heptane plus fractions of light crudes*. Nigerian Annual International Conference and Exhibitions, SPE 111918.
- [10] Katz, D. L., Herzog, R. A., & Hekim, Y. (1981). *Predicting yield of revaporized condensate in gas storage*. Proceedings of Fall SPE Annual Technical Conference. San Antonio, TX, SPE 10166.
- [11] Kay, W. B. (1936). Density of hydrocarbon gases and vapor. *Ind. Eng. Chem.*, 28, 1014-1019.
- [12] Kesler M.G. & Lee B.I. (1976). Improved prediction of enthalpy of fractions. *Hydrocarbon Process*, 55, 153–158.
- [13] Lasater, J.A. (1958). Bubble point pressure correlations. *J. Pet. Technol.*, 10(5), 65–67.
- [14] Naji, H.S. (2011). The dead oil viscosity correlations, A C-sharp simulation approach. *JKAU: Eng. Sci.*, 22(2), 61-87.
- [15] Pedersen, K. S., Fredeslund, A. A., & Thomassen, P. (1989). *Properties of Oils and Natural gases*, Gulf. Available at: <https://trove.nla.gov.au/work/18894087?q&versionId=22179508>.
- [16] Pirson, S.J. (1977). *Oil reservoir engineering*. Huntington, New York: Robert E. Krieger Publishing.
- [17] Riazi M. R. & Daubert, T. E. (1980). Simplify property predictions. *Hydrocarbon Processing*, 115-116.
- [18] Riazi, M. R. & Daubert, T. E. (1987). Characterization parameters for petroleum fractions. *Industrial and Engineering Chemistry*, 26(4), 755-759.
- [19] Riazi, M. R. (1989). Distribution model for properties of hydrocarbon-plus fractions. *Industrial and Engineering Chemistry*, 28, 1731-1735.
- [20] Riazi, M. R. (1996). A continuous model for C7+ fraction characterization of petroleum fluids. *Industrial and Engineering Chemistry*, 36, 4299-4307.
- [21] Riazi, M. R. (2005). Characterization and properties of petroleum fractions. Available at: https://www.astm.org/DIGITAL_LIBRARY/MNL/SOURCE_PAGES/MNL50_foreword.pdf.
- [22] Sim, W. J. & Daubert, T. (1980). Prediction of vapor-liquid equilibria of undefined mixtures, *Ind. Eng. Chem. Process Des. Dev.*, 19(3), 386-393.
- [23] Standing, M.B. (1981). *Volumetric and phase behavior of oil field hydrocarbon systems*. (9th ed.). Richardson, Texas: Society of Petroleum Engineers of AIME.
- [24] Standing, M.B. (1947). A pressure-volume-temperature correlation for mixtures of California oils and gases. *API Drilling and Production Practice*, 275-287.
- [25] Watson, K.M. & Nelson, E.F. (1933). Improved methods for approximating critical and thermal properties of petroleum. *Industrial and Engineering Chemistry*, 25, 880.
- [26] Watson, K.M., Nelson, E.F., & Murphy, G.B. (1935). Characterization of petroleum fractions. *Industrial and Engineering Chemistry*, 7, 1460–1464.
- [27] Whitson, C.H. (1983). Characterizing hydrocarbon plus fractions. *SPE J.*, 23(4), 683-694. Available at: <http://dx.doi.org/10.2118/12233-PA>.
- [28] https://petrowiki.org/Crude_oil_characterization, May, 2020.

Appendix

Statistical Error Analyses Methods

Average Relative Error, (ARE, %):

Average relative error measures the arithmetic average of relative deviation, expressed in percentage, of the estimates from experimental values. The lower the value of ARE, the more equally distributed the errors are between negative and positives values.

$$ARE (\%) = \left(\frac{1}{n} \sum_{i=1}^n E_i \right) * 100$$

Where, $n = \text{number of data points used}$

And $E_i = [(X_{obs} - X_{exp})/X_{exp}]_i$ for $i = 1, 2, 3, \dots, n$

Where,

X_{obs} is observed or estimated value from various methods,

X_{exp} is actual value of parameter obtained by experiments.

The lower the value of ARE, the more equally distributed are the errors between positive and negative values.

Average Absolute Percent Relative Deviation (AARD):

AARD is the absolute value

of Average relative error, expressed in percentage. A lower value implies a better correlation, and is expressed mathematically as follows:

$$AARD, \% = \frac{1}{n} \sum_{i=1}^n |E_i|$$

A lower value implies a better correlation performance.

Absolute Minimum RelativeError($E_{i_{min}}$):

This is the smallest absolute value of relative errors of the estimates made for $i = 1, 2, 3, \dots, n$. A lower value implies a better correlation, and is expressed mathematically as follows:

$$E_{i_{min}} = |E_i|_{\text{minimum}}, i = 1, 2, 3, \dots, n.$$

Absolute Maximum RelativeError($E_{i_{max}}$):

This is the smallest absolute value of relative errors of the estimates made for $i = 1, 2, 3, \dots, n$. A lower value implies a better correlation, and is expressed mathematically as follows:

$$E_{i_{max}} = |E_i|_{\text{maximum}}, i = 1, 2, 3, \dots, n.$$

Relative Mean Square Error (RMSE):

RMSE indicates the

standard deviation of the residuals or how far the points are from the regression or modelled line. A lower value of RMSE means a smaller degree of scatter

$$RMSE = \sqrt{(1/(n-1)) * \sum_{i=1}^n (E_i)^2}$$

Correlation Coefficient, R^2 :

The correlation coefficient, R^2 , represents the degree of success in reducing the standard deviation by regression analysis. It is defined as:

$$R^2 = 1 - \left[\sum_{i=1}^n (X_{obs} - X_{exp})^2 / \sum_{i=1}^n (X_{obs} - X_{avg})^2 \right]$$

Where,

$$X_{avg} = \left(\sum_{i=1}^n X_{i_{exp}} \right) / n$$