

PVT Properties of Live Crude Oils from Upstream Production Platforms

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Abstract: The physical and compositional properties of live crude oils strongly affect the strategy of transportation of oil and gas from reservoirs to the stock tank and their storage. The relevant PVT properties of live crude oils like solution gas-oil ratio and oil formation volume factor should be measured preferably in laboratory for different pressures at the process or reservoir temperature. The sampling and PVT analysis include time consuming or expensive procedures and the data obtained are correlated for interpolation or estimation of properties. These properties vary considerably for different classes of crude oils. We obtain experimental data of crude oils properties from the PVT analysis of primary high-pressure separator samples of 260 live paraffinic-naphthenic crude oils from forty-four Brazilian oil wells. The solution gas-oil ratio and oil formation volume factor were obtained within experimental uncertainties of 5.79% and 1.00%, respectively. We have compared the results with the estimates of several cubic equations of state as well as with widely used literature correlations. The best equation of state estimate solution gas-oil ratio with average absolute percent relative error (AARE) of 10.36%, better than the empirical correlations in the literature using measured temperature, pressure and composition, the empirical correlation for solution gas-oil ratio with parameters estimated from the experimental data shows an AARE of 10.77%. The equations of state and literature correlations estimate the oil formation volume factor with an AARE about 2%, which is lower than the needed accuracy. The measured oil formation volume factors are correlated with an average absolute percent relative error of 1.18%, with a proposed correlation using readily measured liquid densities and solution gas-oil ratio. We can estimate the solution gas-oil ratio by Peng-Robinson equation of state and oil formation volume factor by proposed correlation to the needed accuracy for live paraffinic-naphthenic crude oils under separator conditions from composition, temperature and densities of gas and oil.

Keywords: Live Crude Oils, Experimental PVT Properties, Solution Gas-Oil Ratio, Oil Formation Volume Factor, Paraffinic-Naphthenic Crudes

1. Introduction

The oil and gas are separated from reservoir fluids in one or more stages in upstream production platforms, usually at higher than atmospheric pressures to ensure maximum recovery of oil. The oil separated from reservoir fluids, known as live crude oil, has dissolved gas in solution that may liberate from solution at surface conditions. The oil separated at the primary separator may undergo further separation and is stored or transported to refineries. Physical and compositional properties of live crude oils affect the design and the strategy of transport, storage and blending of crude oils. During the

flow of live crude oils in the pumping system or in the storage tanks, the temperatures and the pressure can vary. Also during the economic production period, the pressure, temperature and composition of oil vary considerably. These changes cause considerable variation of properties of the live crude oils produced in the primary separator. The changing properties of live crude oils should preferably be measured experimentally at various temperatures and pressures in the laboratory by a PVT analysis, which includes procedures which are expensive and time consuming. The experimental measurements can be used to evaluate the reliability of correlations proposed in the literature to estimate these properties.

The PVT properties are also useful for history matching in

reservoir simulations aiming to maximize production. In particular, the solution gas-oil ratio and oil formation volume factor are useful for determining the optimum separator pressure for maximum production of oil. In literature several correlations are proposed to estimate empirically saturation pressure, solution gas-oil ratio, and oil formation volume factor using graphical or regression methods and generally use the process data such as temperature and pressure, API gravity of the oil, fluid composition, molecular weight of the oil constituents as input data. Compared to experimental data, there are some disadvantages in using these correlations to obtain estimates with the required precision like the need for other experimental properties, the limited range of input properties and the type of crude oil produced. The physicochemical nature of live crude oil and its type depends on its origin.

The empirical correlations are used to select proper operating conditions of primary high-pressure separator for improving the recovery of oil and producing stable crude oil with acceptable properties for transporting to refineries or ports. The high costs involved in producing oil from off-shore oil fields demand a careful analysis of correlations with experimental measurements for the type of crude oil produced. Unlike the very expensive reservoir bottom hole samples, the samples of live crude oil from primary separator of off-shore platforms are more readily available. The cost of bottom hole sampling reservoir fluids is prohibitive for off-shore oil wells, limiting the number of samples available to the initial production period. The composition of the reservoir fluid entering the primary separator can be readily calculated, when necessary, by combining the composition of the oil and the composition of the gases produced. Tests are needed to determine the amount and properties of oils which can be produced at the surface conditions [1].

There is little published work on the PVT properties of live oils, especially paraffinic-naphthenic crudes like the off-shore oil produced in Brazil. In this work, we measure the solution gas-oil ratio and oil formation volume factor of live paraffinic-naphthenic crude oils from high pressure separators of several Brazilian off shore oil wells and evaluate the cubic equations of state and empirical literature correlations using experimental data.

2. Experimental Methodology

The live crude oil samples were obtained from primary high-pressure separator located in off-shore platforms. The samples were taken during stationary state at operating temperature and pressure of the separator using standard procedures by the operators.

The primary separator samples of live crude oil from production platforms are received in the laboratory in small high-pressure sampling cylinders equipped with floating pistons along with the sampling and operating conditions. The samples are restored to original conditions of the primary separator and pressure is slightly increased to guarantee a single phase. A sample of the oil is collected from the sampling cylinder to the pycnometer and the

volume and mass of the live oil is recorded. The gas dissolved in the oil is released from the pycnometer to the gasometer where the volume of liberated gas is measured under standard conditions. The pycnometer with the residual oil is weighed and the mass of the dead oil is obtained. The density of residual oil is measured in densimeter (Anton Parr, DMA 4500M) according to ASTM D5002-99 [2] and the water content is measured using Karl Fischer Titration for moisture determination (Metrohm, 852 Titrando) following procedure ASTM D4928-12 [3].

The results of the data collected allow the calculation of the gas oil ratio and the subsequent oil formation volume factor. The solution gas-oil ratio is defined as the volumetric ratio of the total gas liberated to the stock tank oil, both at standard conditions. The oil formation volume factor is calculated as the ratio of the volume of oil plus gas dissolved at separator conditions of pressure and temperature to the volume of the residual oil at standard conditions.

In order to obtain the composition of the oil, we measured the density of dead oil at standard conditions with densimeter (Anton Paar, DMA 4500 M) following procedure ASTM 5002-99 [2] and the composition of the dead oil and liberated gas from the live oil using chromatographs (Agilent Technologies, 7890A) following procedure ASTM D2887-03 [4] and ASTM D1945-03(2010) [5] at standard conditions. The Table 1 shows representative compositions of the samples of paraffinic-naphthenic crude oils studied. Figure 1 shows composition of oils representative of samples studied, presented in Table 1.

Table 1. Experimental values of composition of paraffinic-naphthenic oil.

Component	Average mole fraction, mol%			
	Sample 1	Sample 2	Sample 3	Sample 4
CO ₂	3.2946	0.0010	4.4809	1.3185
H ₂ S	0.0000	0.0000	0.0000	0.0000
N ₂	0.0459	0.0566	0.0264	0.3804
CH ₄	5.0711	5.6769	7.2628	5.9534
C ₂ H ₆	2.2625	0.8619	3.1839	2.9430
C ₃ H ₈	3.0345	0.7416	3.4816	3.6392
i-C ₄	0.9881	0.2258	0.8827	1.0581
n-C ₄	2.7204	0.3600	2.1756	2.5763
i-C ₅	1.4790	0.1922	1.1567	1.3912
n-C ₅	2.3443	0.2881	1.8380	2.1464
C ₆	3.8923	1.4421	3.2808	3.6914
C ₇	5.9374	3.6888	5.2565	5.7144
C ₈	6.8520	6.7416	6.3493	6.7145
C ₉	5.5747	6.7449	5.2263	5.3878
C ₁₀	4.8269	6.1569	4.6385	4.7179
C ₁₁	3.8181	4.9336	3.8045	3.7736
C ₁₂	3.4462	4.7231	3.3756	3.4128
C ₁₃	3.1596	4.7998	3.1135	3.1030
C ₁₄	2.9191	4.6150	2.8752	2.8869
C ₁₅	2.7905	4.5020	2.7084	2.7950
C ₁₆	2.1059	2.9465	2.1604	2.2065
C ₁₇	1.7892	2.9129	1.6918	1.8018
C ₁₈	1.9111	3.0303	1.8586	1.9568
C ₁₉	1.6526	2.7546	1.6362	1.7113
C ₂₀	1.3416	2.1553	1.3423	1.4011
C ₂₁	1.1996	1.8408	1.2073	1.2567
C ₂₂	1.1190	1.5600	1.1517	1.1617
C ₂₃	1.0518	1.3746	1.0087	1.0885
C ₂₄	0.9684	1.1191	0.9213	0.9694

Average mole fraction, mol%				
Component	Sample 1	Sample 2	Sample 3	Sample 4
C25	0.8347	0.9983	0.8816	0.9391
C26	0.8429	0.8028	0.8419	0.8867
C27	0.7931	0.7553	0.8260	0.8176
C28	0.8709	0.6801	0.7784	0.8921
C29	0.8219	0.5774	0.7625	0.8361
C30+	18.2403	19.7400	17.8140	18.4707

2.1. Characterization of Crude Oil

Paraffinic-naphthenic oil samples were obtained from forty-four different oil wells of the Santos Basin of Brazil.

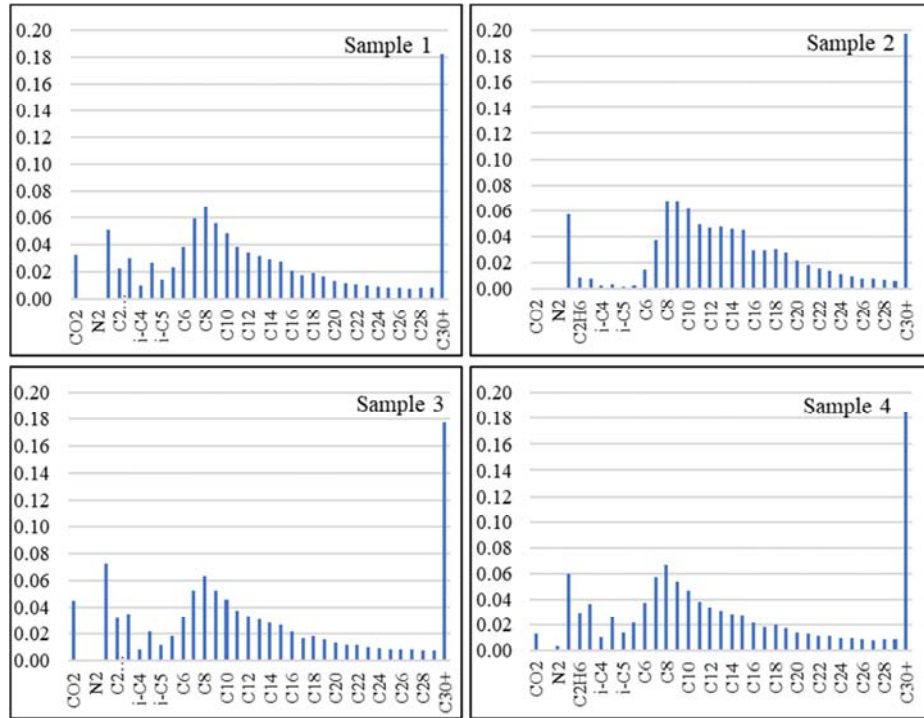


Figure 1. Composition of samples of paraffinic-naphthenic oil.

For confirmation, six of the crude oil samples were characterized by Density-Viscosity Ratio proposed by Farah [6] by means of a relationship $API(A/B)$ based on A and B parameters of Walther-ASTM equation. Table 2 from reference [6] shows the classification of oil and its fractions based on this relationship.

Table 2. Classification of oil and its fractions based on the relationship of Walther-ASTM, Farah [6].

API(A/B)	Type
>14	Paraffinic
12-14	Paraffinic-naphthenic
10-12	Naphthenic
8-10	Aromatic-intermediate
6-8	Aromatic-naphthenic
<6	Aromatic-asphaltic

The Walther-ASTM relationship has been used for crude oil sample characterization by taking into account the temperature dependence of the crude oil kinematic viscosity. We have also determined the paraffinic, naphthenic and, aromatic contents of each crude oil sample.

In the Walther-ASTM relationship, A/B represents the decimal logarithm of temperature for which the value of variable z is $10 \text{ mm}^2\text{s}^{-1}$. The values of A and B were obtained by plotting $\log_{10}(\log_{10}(z))$ vs. $\log_{10}(T)$, Equation 1, where z is

obtained from values of kinematic viscosity and temperature, Equation 2. In Equation 2 the parameter A is equal to $\log_{10}(\log_{10}(z))$ when the temperature tends to 1 K and the parameter B represents the dependence of viscosity with the temperature as presented in Equation 1.

$$\log_{10}(\log_{10}(z)) = A - B \times \log_{10}(T) \quad (1)$$

$$z = v + 0.7 + C - D + E - F + G - H \quad (2)$$

Where v is the kinematic viscosity in mm^2s^{-1} , T is the temperature in K and C, D, E, F, G, H are the model fitted parameters: $C = e^{(-1.14883 - 2.65868 \times v)}$, $D = e^{(-0.0038138 - 12.5645 \times v)}$, $E = e^{(5.46491 - 37.6289 \times v)}$, $F = e^{(13.0458 - 74.6851 \times v)}$, $G = e^{(37.4619 - 192.643 \times v)}$ and $H = e^{(80.4945 - 400.468 \times v)}$.

The kinematic viscosities were obtained experimentally using capillary tube viscometer at different temperatures, ASTM D445-06 [7]. We have measured the viscosities for three different temperatures for six crude oils samples. These experimental values were used in Equation 2 for calculating z . Afterwards, a plot of $\log_{10}(\log_{10}(z))$ vs. $\log_{10}(T)$ is used for fitting both the parameters A and B by means of the linear relationship represented by Equation 1.

All the six samples tested of crude oil samples were found to be paraffinic-naphthenic based on the calculated values of $API(A/B)$ for these oils which lies between 12 and 14, Table 3.

Table 3. Oil gravity API, temperature T, kinematic viscosity ν , and calculated parameters A and B for characterization of the crude oil by means of the relationship $API/(A/B)$ for crude oil.

API	T	ν	$\log(T)$	$\log_{10}(\log_{10}(z))$	A	B	API/(A/B)
33	303.15	8.016	2.481443	-0.027	10.3	4.18	13
	313.15	5.920	2.495544	-0.086			
	333.15	3.600	2.522444	-0.198			
29	313.15	9.198	2.495544	-0.002	10	4	12
	328.15	6.156	2.515874	-0.078			
	343.15	4.194	2.535294	-0.161			
33	313.15	7.664	2.495544	-0.035	11.31	4.55	13
	328.15	4.720	2.515874	-0.134			
	343.15	3.360	2.535294	-0.216			
30	321.15	13.162	2.506708	0.058	13.101	5.204	12
	326.15	10.330	2.513417	0.018			
	331.15	8.707	2.520025	-0.012			
33	311.15	12.040	2.492970	0.043	7.4513	2.9718	13
	316.15	10.470	2.499893	0.020			
	321.15	9.440	2.506708	0.003			
32	323.15	11.447	2.509404	0.035	8.87	3.521	13
	329.15	9.351	2.517394	0.001			
	335.15	8.295	2.525239	-0.020			
33	341.15	7.094	2.532945	-0.050	10.3	4.18	13
	303.15	8.016	2.481443	-0.027			
	313.15	5.920	2.495544	-0.086			
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The oil API gravity was calculated from standard density by Equation 3, the densities were also measured at the standard temperature of 288.71 K.

$$API = (141.5/d_o) - 131.5 \quad (3)$$

Where d_o is oil specific gravity (water=1) at 288.71 K.

2.2. Experimental Data of Live Oil Properties

Experimental data of fluid properties of 260 primary high pressure separator samples of paraffinic-naphthenic live crude oil were obtained. The conditions of separation, temperature and pressure, and the experimental properties obtained are presented in Table 4.

Table 4. Data ranges for samples.

	Maximum	Minimum	Average
P, psia	290	111	230
T, deg F	172	81	126
API, °API	34	22	30
RS, scf/STB	156	19	79
Bo, bbl/STB	1.116	1.001	1.042

For each sample PVT tests were repeated three or more times. The experimental error is estimated to be approximately the uncertainty in measurements and is shown in Table 5.

Table 5. Uncertainty in measurements.

fluid property	Experimental uncertainty	Experimental uncertainty, %
water content, %	± 0.244	5.00
ρ_o , kg/m ³	± 0.946	31.43
R_s , SCF/STB	± 0.612	1.00
B_o , bbl/STB	± 0.060	5.79

3. Results and Discussion

Frequently used literature correlations for solution gas-oil ratio and oil formation volume factor were evaluated in their ability to represent the experimental data and the estimated values showed large deviations (see section 3.1). To better represent our experimental data, we proposed new correlations and re estimating the parameters from a part of

experimental data. We measured composition of the samples to apply equations of states of Peng-Robinson and Soave-Redlich-Kwong. These equations were evaluated for their ability to calculate the values of solution gas-oil ratio and oil formation volume factor.

3.1. Comparison Between Estimated and Experimental Values

For the purpose of evaluation, average, maximum and minimum average absolute percent relative error, AARE, and percent absolute standard deviation, SDA, were calculated between estimated values on comparison with experimental values.

AARE - average absolute percent relative error. The lower value of AARE represents the better correlation between evaluated correlations. AARE is defined by Equation 4:

$$\text{AARE} = 100/\text{ND} \times \sum_{i=1}^{\text{ND}} (|(X_{\text{est}} + X_{\text{exp}})/X_{\text{exp}}|) \quad (4)$$

Table 6. Statistical accuracy of solution gas-oil ratio correlations and cubic equations of state.

Correlation	Average AARE, %	Maximum AARE, %	Minimum AARE, %	SDA, %
Proposed	10.77	66.14	0.01	11.34
Standing	44.26	87.09	2.28	14.84
Glaso	34.60	128.16	1.13	18.11
Vazquez and Beggs	45.94	90.42	3.59	17.26
Kartoatmodjo and Schmidt	34.00	82.25	0.54	17.34
Petrosky and Farshad	38.90	552.89	0.02	64.42
Elsharkawy and Alikhan	36.56	124.94	1.56	18.66
Al-Marhoun	64.22	260.28	3.89	24.46
Peng-Robinson EOS	10.36	22.92	0.56	6.05
Soave-Redlich-Kwong EOS	16.68	28.76	0.00	7.38

For solution gas-oil ratio, the value of AARE is in the range from 34.00% for Kartoatmodjo and Schmidt correlation to 64.22% for Al-Marhoun correlation. The Peng-Robinson EOS and Soave-Redlich-Kwong EOS presented better results than the correlations found in the literature for

SDA - percent absolute standard deviation. SDA is a measure of dispersion and is defined by Equation 5:

$$\text{SDA} = \sqrt{(1/(\text{ND}-1) \sum (\text{AARE} - (\text{AARE})^{\sim})^2)} \quad (5)$$

The statistical results of gas-oil ratio and oil formation volume factor are shown on Tables 6 and 7, respectively.

Seven literature correlations for solution gas-oil ratio were for their ability to represent our measured experimental values: Standing [8], Glaso [9], Vazquez and Beggs [10], Kartoatmodjo and Schmidt [11], Petrosky and Farshad [12], Elsharkawy and Alikhan [13], Al-Marhoun [14].

Eight literature correlations for oil formation volume factor were evaluated for their ability to represent our measured experimental values: Standing [8], Glaso [9], Vazquez and Beggs [10], Kartoatmodjo and Schmidt [11], McCain [15], Petrosky and Farshad [12], Omar and Todd [16], Elsharkawy and Alikhan [13].

the estimation of the gas-oil ratio. While Peng-Robinson EOS and Soave-Redlich-Kwong EOS presented errors of 10.36% and 16.68%, respectively, the smallest errors found by the correlations are 34.00% and 34.60% for Kartoatmodjo and Schmidt correlation and Glaso correlation, respectively.

Table 7. Statistical accuracy of oil formation volume factor correlations and cubic equations of state.

Correlation	Average AARE, %	Maximum AARE, %	Minimum AARE, %	SDA, %
Proposed	1.18	6.02	0.02	0.97
Standing	2.29	7.12	0.00	1.52
Glaso	2.99	9.20	0.05	1.62
Vazquez and Beggs	2.59	18.16	0.01	2.32
Kartoatmodjo and Schmidt	2.76	7.99	0.01	1.65
McCain	2.14	6.84	0.03	1.47
Petrosky and Farshad	2.69	7.47	0.05	1.56
Omar and Todd	1.97	11.25	0.00	1.64
Elsharkawy and Alikhan	7.09	18.37	0.22	3.02
Peng-Robinson EOS	2.73	11.76	0.25	2.09
Soave-Redlich-Kwong EOS	2.72	11.74	0.26	2.08

For oil formation volume factor, the value of AARE is in the range from 1.97% for Omar and Todd correlation to 7.09% for Elsharkawy and Alikhan correlation. For oil formation volume factor, Peng-Robinson EOS and Soave-Redlich-Kwong EOS presented errors of 2.73% and 2.72%, respectively, while the correlations presented 1.97% and 2.14% for Omar and Todd correlation and McCain correlation.

The estimated values by literature correlations show large deviations from experimental values of solution gas-oil ratio and oil formation volume factor. The equations of state present good results for the estimation of the solution gas-oil ratio and less satisfactory results for the estimation of the oil formation volume factor. The equations of state were developed to describe the relationship between pressure, molar volume and temperature of gases and phase

equilibrium, and do not predict liquid density accurately, leading to good solution gas-oil ratio calculations because this is an important phase equilibrium property for estimating the production of reservoir, calculated as the ratio of the volume of the total gas liberated to the volume of the residual oil, both at standard conditions. The equations of state present major errors in oil formation volume factor calculations because this is an important volumetric property

in the production of petroleum, calculated as the ratio of the volume of oil plus gas dissolved at separator conditions of pressure and temperature to the volume of the residual oil at standard conditions.

The crossplots are presented in Figures 2 and 3 for empirical correlations and in Figures 4 and 5 for equations of state. In the crossplot, the estimated values are around plot as a straight line with a slope of 45° indicating the accuracy of models.

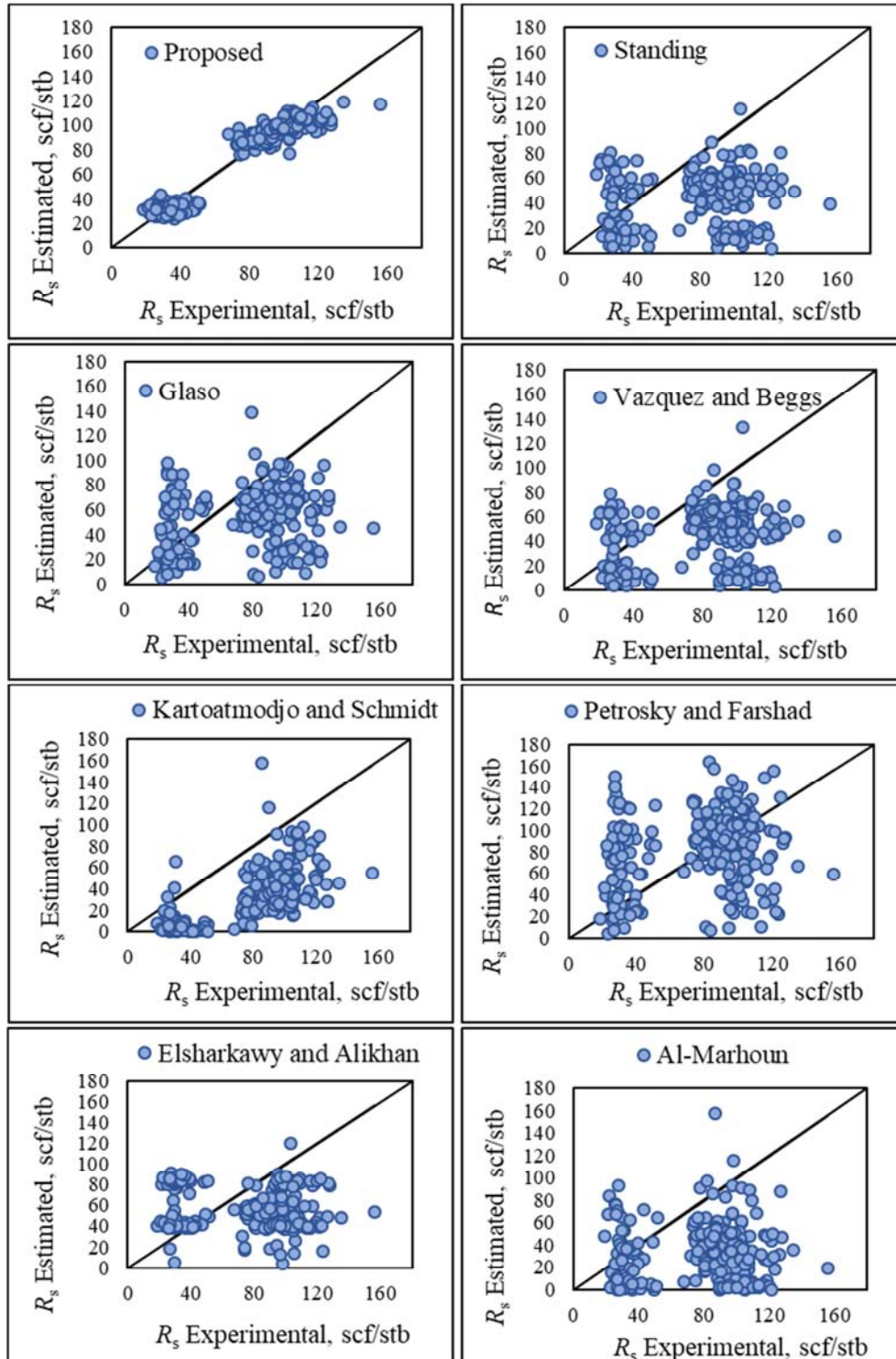


Figure 2. Crossplot solution gas-oil ratio correlations.

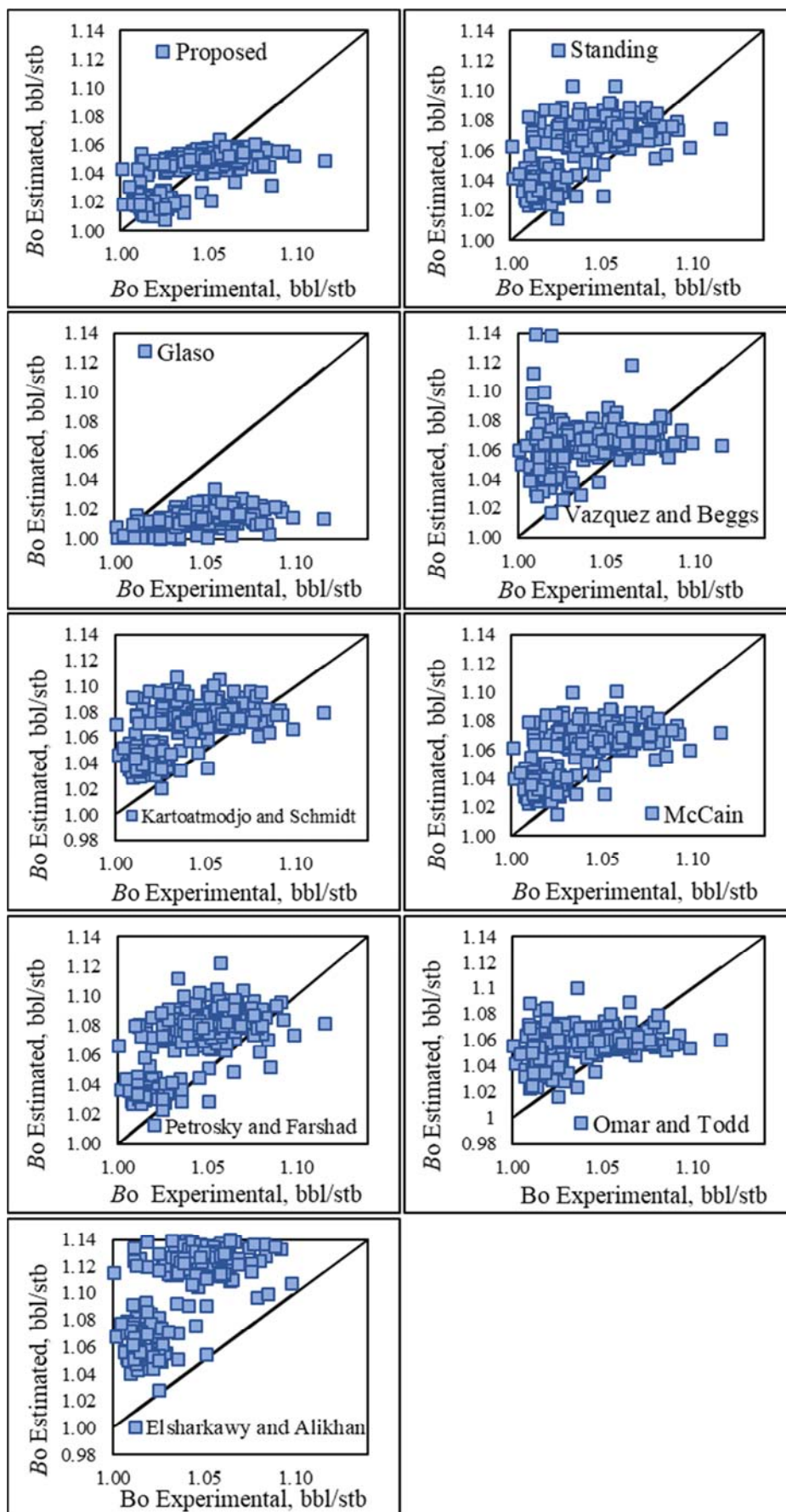


Figure 3. Crossplot oil formation volume factor correlations.

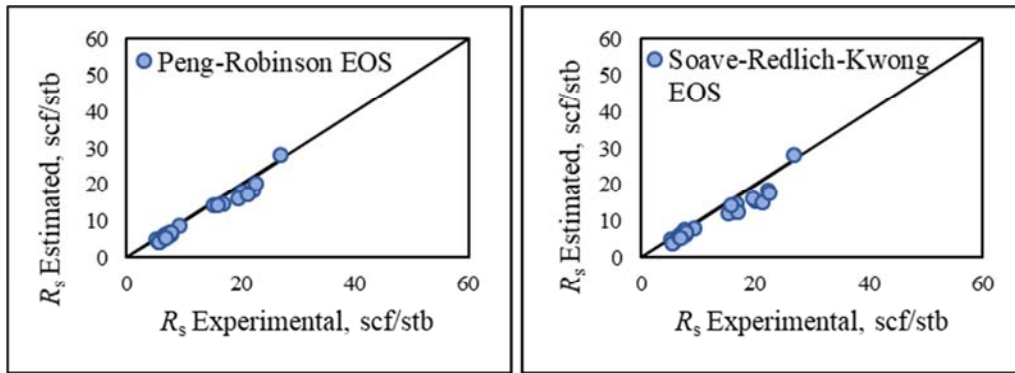


Figure 4. Crossplot solution gas-oil ratio calculated by Peng-Robinson EOS and Soave-Redlich-Kwong EOS.

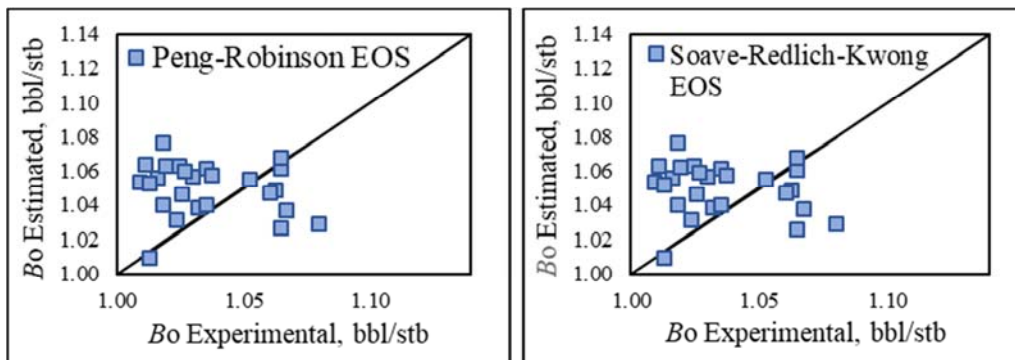


Figure 5. Crossplot oil formation volume factor calculated by Peng-Robinson EOS and Soave-Redlich-Kwong EOS.

3.2. Proposed Correlations

New empirical correlations were developed to estimate solution gas-oil ratio and oil formation volume factor using 260 experimental values of PVT properties with acceptable deviations from the measured values using open R software. [R Core Team (2016). R: A language and environment for statistical computing. R Foundation for Statistical

Computing, Vienna, Austria. URL <https://www.R-project.org/>].

The solution gas-oil ratio correlation developed from our data is shown below in Equation 6. The following model is proposed for solution gas-oil ratio as a function of gas specific gravity, separator pressure, dead oil API gravity, and temperature.

$$\log_{10}(R_s) = -0.81251 - 0.04465 \times \log_{10}(d_g) + 1.56535 \times \log_{10}(P) + 0.25354 \times \log_{10}(API) - 0.66027 \times \log_{10}(T) \quad (6)$$

Where: API, °API; B_o , bbl/STB; d_o , oil specific gravity (water=1); d_g , gas specific gravity (air=1); P, psia; R_s , scf/STB; T, deg F.

The newly proposed correlation of our data shows the lowest error 10.77% in comparison with literature correlations, Table 6. The correlations poorly estimate the solution gas-oil ratio compared to cubic equations of state as the variation of composition is not taken into account directly.

The proposed oil formation volume factor correlation is shown below in Equation 7. The following model is proposed for oil formation volume factor as a function of gas specific gravity, oil specific gravity, and temperature:

$$\log_{10}(B_o) = -0.008399 - 0.007717 \times \log_{10}(T) + 0.005794 \times \log_{10}(d_g/d_o) + 0.023053 \times \log_{10}(R_s) \quad (7)$$

Where: B_o , bbl/STB; d_o , oil specific gravity (water=1); d_g , gas specific gravity (air=1); P, psia; R_s , scf/STB; T, deg F.

The newly proposed correlation shows the lowest error 1.18% in comparison with literature correlations, Table 7. The cubic equations of state estimate the oil formation volume factor with less accuracy as they do not estimate the variation of liquid density with the required precision from temperature, pressure and composition.

4. Conclusions

The samples were characterized by the variation of viscosity with temperature and were classified as paraffinic-naphthenic. The methodology for restoration of samples and measurement of solution gas-oil ratio and oil formation volume factor was found to be effective and rapid. The solution gas-oil ratio and oil formation volume factor correlations found in literature were found to estimate the properties live paraffinic-naphthenic crude oils with large

deviations. Both these properties can be estimated to the needed precision by the newly proposed correlations. The solution gas-oil ratio can be estimated accurately by Peng-Robinson equation of state using temperature, pressure and measured composition as input parameters.

Nomenclature

ρ_o	density of oil, kg/m ³
d_o	oil specific gravity (water=1)
d_g	gas specific gravity (air=1)
API	oil API gravity, °API
P	pressure, psia
T	temperature, deg F
B_o	oil formation volume factor, bbl/STB
R_s	solution gas oil ratio, scf/STB
X_{exp}	experimental variable
X_{est}	estimated variable
ND	number of data sets

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