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Improved Characterization of Heptanes-Plus Fractions Of Light Crudes

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Abstract

Heptanes plus fractions have strong effects on the physical properties and phase behaviour of petroleum fluids. It is therefore very important to properly characterize plus fractions. A step to achieving improved characterization is to obtain more realistic molecular weights. Most of the current methods of heptanes plus characterization assume their molecular weights are accurate. However, what is commonly measured in the laboratory is the molecular weight of the complete fluid; the molecular weight of the heptane-plus fraction is then estimated using Kay's mixing rule. Unfortunately, physical properties like molecular weight obtained using 'equivalent fluid' principles by mixing pure components, do not give the same values with actual measurements. Therefore, while a very accurate estimate of the molecular weight of a reservoir oil could be available, that of the heavy fractions, which is 'inferred' could be unreliable, because of the mixing rule.

A simple technique has been formulated to achieve improved characterization of petroleum fluids and the heavy fractions. We suggest 'fine tuning' Kay's mixing rule in order to achieve a match between actual measured molecular weight and the 'equivalent fluid'. Experimental data from over 400 PVT reports from

over 100 fields in the Niger Delta were collected and studied. A correlation was established between oil gravity and molecular weight and, compared with other commonly used correlations. Statistical error analysis was undertaken. Heptanes plus molecular weights which were generally estimated using Kay's mixing rule were found to be generally high and hence fine tuned using a simple technique.

The results of this study show that the well-known Cragoe's and Standing correlations gave absolute average deviation of 126.8 and 53.3 respectively for light crudes, compared to 2.5 obtained in this study. Furthermore, better description of heavy fractions was achieved with more accurate molecular weight.

It is concluded that the proposed technique perhaps provides a theoretical basis for the usual 'tuning' of heptane-plus properties during fluid modelling. It is also concluded that a more accurate correlation for estimating the molecular weight of light crudes has been developed.

Introduction

Accurate description of reservoir fluid systems is a key element of petroleum reservoir characterization and management. The aim is often to predict the properties and behaviour of fluids at any temperature and pressure, to promote best engineering and reservoir management practices. Basic information for-reservoir fluid characterization may be obtained from laboratory analysis, use of mathematical models or approximate correlations. Experimental data, however are very expensive, time consuming and difficult to reproduce for near critical fluids. The use of mathematical models could be fast, but they require some degree of expertise. They also often require some experimental data for fine-tuning or calibration. Correlations, on the other hand, often require little expertise to use and could be

very useful as quick surveillance tools in new fields and in areas with sparse experimental data.

As noted by Dindoruk and Christman⁽¹⁾, PVT property correlations could be generic based on randomly selected data sets, or they could be specialized representing a type of oil or geographic area.

A number of techniques are available for accurate measurement of molecular weights of hydrocarbons. These are largely based on the principles of boiling point elevation, freezing point depression, vapour phase osmosis or chromatography, with the freezing point depression method preferred as the most accurate technique. However, the molecular weight of the heavy fractions can only be inferred from the measured values for the complete fluid.

Theoretical Framework

The physical properties of fluids can be related to their intermolecular forces and molecular size i.e.

$$\theta = f(\text{intermolecular forces, molecular size})$$

It is perhaps with this in view that Riazi and Daubert⁽²⁾ proposed a generalized physical property correlation in the form:

$$\theta = aT_B^b \gamma^c \quad (1)$$

Where, θ is any physical property such as molecular weight, T_B is the normal boiling point and a , b , and c are empirical constants.

However, for a quick-look description of molecular weight, we can simplify equation (1), by setting $b = 0$ to obtain

$$M \cong a\gamma^c \quad (2)$$

Eqn. (2) is the basis of the correlation developed by such authors as Cragoe⁽³⁾, Kesler-Lee⁽⁴⁾ and Standing⁽⁵⁾.

The Molecular weight M is composition dependent. Hence,

$$M = f(X_i) \quad (3)$$

Where,

$$X_i = \text{Mole fraction of components } i.$$

For a multi-component hydrocarbon system, equation (3) is normally expressed using Kay's mixing rule as:

$$M = \sum X_i M_i \quad (4)$$

Where,

M_i = Molecular weight of the pure components.

As noted by Kreglewski⁽⁶⁾ and several other workers, equation (4) is not very accurate. It can be improved upon by use of a better mixing rule.

Therefore, using a method similar to the way Equations of state parameters are normally adjusted, we propose 'matching' the actual experimental values with the 'equivalent fluid' obtained from the mixing of pure components. Thus, we propose an expression of the form:

$$M = (1+\Psi) \sum X_i M_i \quad (5)$$

Where,

M = Actual molecular weight measured

X_i = Mole fraction of component i .

M_i = Molecular weight of component i

Ψ = Substance-dependent adjustment factor

Expanding the equation above, we have:

$$M/(1+\Psi) = \sum^6 X_i M_i + x_{7+} M_{7+} \quad (6)$$

Or,

$$x_{7+} M_{7+} = M/(1+\Psi) - \sum^6 X_i M_i \quad (7)$$

From the fractional compositional data and measured molecular weights, the actual molecular weight of the heptane plus fractions can be established.

However, where compositional data are not available, molecular weight can be established from surface oil gravity data.

Data Collection

Laboratory data on composition and molecular weights from 400 PVT reports and about 100 fields cutting across the entire Niger Delta were collected and analyzed after normal quality checks.

Data range is as shown in Table 1, with depths ranging between 4100 ft and 12,400 ft-ss, and reservoir pressures ranging between 1768 and 8356 psia. Mean values are as shown in Table 2.

Results and Discussion

It is known that unless an accurate mixing rule is employed, a property such as molecular weight of an 'equivalent fluid' obtained from mixing pure components is not the same as the actual property of a

multi-component fluid ⁽⁶⁾. This is demonstrated in Tables 3 and 4, where Kay's rule applied to the critical properties of binary mixtures did not replicate accurately the measured values obtained from Horstman et al ⁽⁷⁾. Maximum deviation is obtained at about 0.5 moles of each fraction.

For Niger Delta crude oil, the adjustment factor Ψ was established at 0.15.

Accurate estimation of the molecular weight of heavy fractions should make tuning of equation of state parameters less necessary. Whitson ^(8,9) has demonstrated that the tuning of equation of state parameters is theoretically same as changing the molecular weight of heptanes plus fractions.

Where compositional data are not available, the correlation for specific gravity was established as:

$$M = 9260.1(\text{API})^{-1.2894} \quad (8)$$

Where,

$$\text{API} = 141.5/\gamma_o - 131.5 \quad (9)$$

And,

$$\gamma_o = \text{Oil Specific gravity at } 60/60 \text{ }^\circ\text{F}$$

Where it is desired to estimate the molecular weight of the heptanes fraction using only oil gravity, equation 10 was developed for Niger Delta fluids:

$$M_{7+} = 459.75 - 16.67 \text{ API} + 0.1778 \text{ API}^2 \quad (10)$$

Where, API is the API gravity of the whole fluid at 60/60.

The true boiling point for the heptanes plus fraction can be estimated using an approximation of a straight chain hydrocarbon:

$$T_B = 25.525 M_{7+}^{0.5739} \quad (11)$$

These correlations were found to be valid for API gravity less than 55. Above this value, Cragoe's formula should be used. Table 5 shows the comparison between this study with Cragoe and Standing correlations. Cragoe's and Standing correlations gave absolute average deviation of 126.8 and 53.3 respectively for light crudes, compared to 2.5 in this study. This is illustrated in Figure 1. Figure 2 shows the relationship between molecular weight and GOR in the Niger Delta, while Figures 3 and 4 show the effects of C7+ fractions on molecular weight and on GOR. They confirm the observation by Wu and Fish ⁽¹⁰⁾, that heptanes plus fraction controls several properties of

hydrocarbon fluids. Figures 3 and 4 suggest that the percentage cut of the heavy fraction present is perhaps more important than the molecular weight of the heavy fractions.

Conclusions

Improved correlations for predicting the molecular weight of Niger Delta crude oils and the heptanes plus fractions have been developed.

The correlations employ simple relationships, while there results were more accurate for the Niger Delta oils than other correlations that used data from other regions of the world.

Nomenclature

a, b, c = Empirical constants defined by equation 1

API = American Petroleum Institute (gravity)

GOR = Gas - Oil Ratio

M = Molecular weight

P = Pressure

T = Temperature

X = Mole fraction

γ = Specific gravity

Ψ = Adjustment factor

Subscripts

B = Boiling point

C = Critical

i = Component

O = Oil

Acknowledgments

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Table 1: Ranges of Data used

Property	Range	
	Oil	Condensate
No of fields	100	15
No of PVT Reports	400	25
Static Reservoir Pressure (psia)	1768 – 5499	2330 – 8356
Reservoir Depths (ft-ss)	4100 – 12400	4100 - 12400
Reservoir Temperature (°R)	518 – 720	590 – 722
Gas-Oil Ratio (scf/stb)	43 – 7425	3,000 – 20,000
Specific oil Gravity	0.716 – 0.95	0.36 – 0.78

Table 2: Mean Composition of petroleum fluids in the Niger Delta

Component	Crude Oils	Condensate
	(mole %)	(mole %)
N ₂	0.13 ± 0.10	0.42 ± 0.40
CO ₂	0.72 ± 0.68	1.47 ± 1.00
C ₁	43.24 ± 11.40	82.52 ± 9.77
C ₂	4.22 ± 2.30	5.54 ± 1.91
C ₃	3.00 ± 2.75	2.89 ± 2.46
iC ₄	1.24 ± 0.98	1.01 ± 0.53
nC ₄	1.70 ± 1.42	1.01 ± 1.02
i-C ₅	1.00 ± 0.80	0.55 ± 0.39
n-C ₅	0.80 ± 0.70	0.43 ± 0.34
C ₆	1.70 ± 1.23	0.61 ± 0.41
C ₇₊	42.00 ± 15.25	3.62 ± 2.89

**TABLE 3: Deviation of Kay's Mixing Rule for Ethane-Propane System ⁽⁷⁾
Ethane(1) –Propane(2)**

x1	X2	EXPERIMENTAL		CALCULATED		DEVIATION	
		Tc (K)	Pc (mPa)	Tc (K)	Pc (mPa)	Tc (K)	Pc (mPa)
0.0000	1.0000	369.70	4.250	369.7000	4.250000	0.000000	0.000000
0.1202	0.8798	363.96	4.447	361.9723	4.325846	1.987658	0.121154
0.2398	0.7602	358.00	4.647	354.2833	4.401314	3.716742	0.245686
0.3598	0.6402	352.45	4.798	346.5685	4.477034	5.881542	0.320966
0.4803	0.5197	344.06	4.960	338.8215	4.553069	5.238487	0.406931
0.5807	0.4193	337.91	5.030	332.3668	4.616422	5.543203	0.413578
0.6603	0.3397	333.05	5.061	327.2493	4.666649	5.800687	0.394351
0.7389	0.2611	327.48	5.076	322.1961	4.716246	5.283881	0.359754
0.8205	0.1795	321.38	5.065	316.9501	4.767736	4.429945	0.297265
0.8997	0.1003	314.10	5.017	311.8583	4.817711	2.241713	0.199289
1.0000	0.0000	305.41	4.881	305.4100	4.881000	0.000000	0.000000

TABLE 4: Deviation of Kay's Mixing Rule for Ethane-n-Butane System ⁽⁷⁾

Ethane(1) –n-Butane(2)							
		EXPERIMENTAL		CALCULATED		DEVIATION	
x1	X2	Tc (K)	Pc (mPa)	Tc (K)	Pc (mPa)	Tc (K)	Pc (mPa)
0.0000	1.0000	424.92	3.790	424.9200	3.790000	0.000000	0.000000
0.1496	0.8504	415.72	4.285	407.0413	3.953214	8.678696	0.331786
0.2990	0.7010	403.82	4.810	389.1865	4.116209	14.63349	0.693791
0.4402	0.5598	390.67	5.266	372.3117	4.270258	18.35830	0.995742
0.5605	0.4395	377.54	5.598	357.9346	4.401506	19.60536	1.196495
0.6601	0.3399	364.38	5.749	346.0314	4.510169	18.34855	1.238831
0.7407	0.2593	352.55	5.813	336.3989	4.598104	16.15106	1.214896
0.8185	0.1815	340.15	5.701	327.1011	4.682984	13.04894	1.018017
0.9095	0.0905	324.39	5.413	316.2257	4.782265	8.164345	0.630736
1.0000	0.0000	305.41	4.881	305.4100	4.881000	0.000000	0.000000

Table 5: Comparison of this study with Others

SAMPLE	API	EXPT MW	THIS STUDY	CRAGOE	STANDING
1	22.30	159.08	169.04	370.88	189.93
2	23.99	231.20	153.85	336.23	186.21
3	45.38	50.60	67.66	154.12	139.18
4	45.38	63.80	67.66	154.12	139.18
5	45.38	46.33	67.66	154.12	139.18
6	19.03	229.79	207.42	463.30	197.13
7	36.95	79.80	88.17	195.93	157.70
8	19.03	126.25	207.42	463.30	197.13
9	17.45	193.04	232.02	526.87	200.62
10	38.98	73.71	82.29	183.91	153.24
11	41.06	83.98	76.96	173.03	148.67
12	41.06	68.07	76.96	173.03	148.67
13	41.06	74.96	76.96	173.03	148.67
14	45.38	53.30	67.66	154.12	139.18
15	20.65	181.06	186.70	412.46	193.57
16	34.97	95.68	94.66	209.28	162.06
17	23.99	148.68	153.85	336.23	186.21
18	34.97	91.34	94.66	209.28	162.06
19	36.95	96.45	88.17	195.93	157.70
20	45.38	54.01	67.66	154.12	139.18
21	22.30	120.67	169.04	370.88	189.93
22	20.65	150.70	186.70	412.46	193.57
23	19.03	178.82	207.42	463.30	197.13
24	22.30	161.70	169.04	370.88	189.93
25	22.30	130.50	169.04	370.88	189.93
26	31.14	139.10	109.92	241.01	170.48
27	54.68	34.90	53.19	124.71	118.69
28	38.98	84.60	82.29	183.91	153.24
29	45.38	50.33	67.66	154.12	139.18

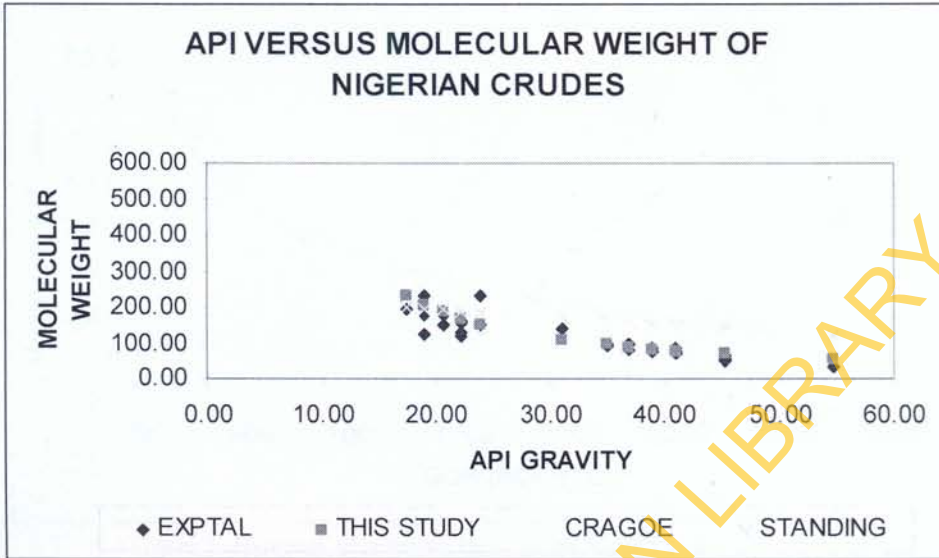


Figure 1: API Gravity Correlation of Molecular Weight

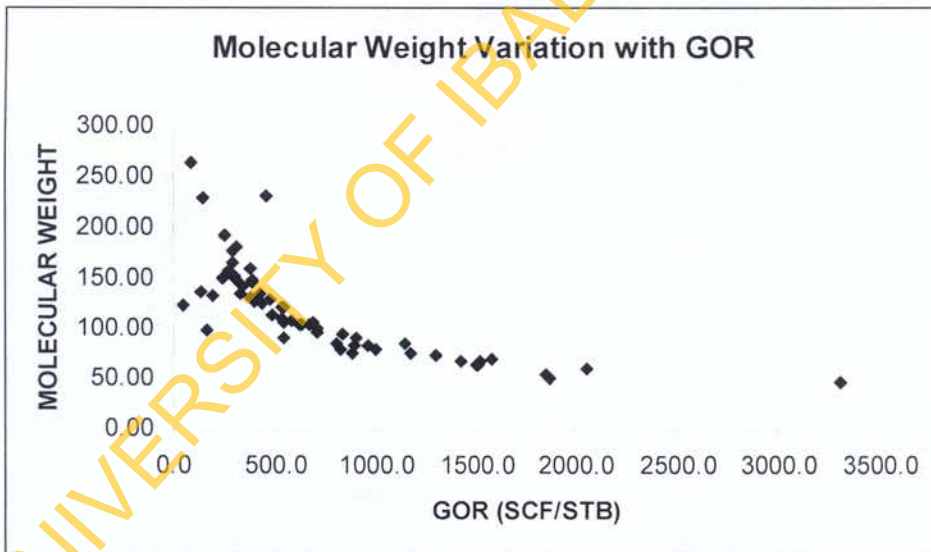


Figure 2: Molecular Weight vs GOR in the Niger Delta

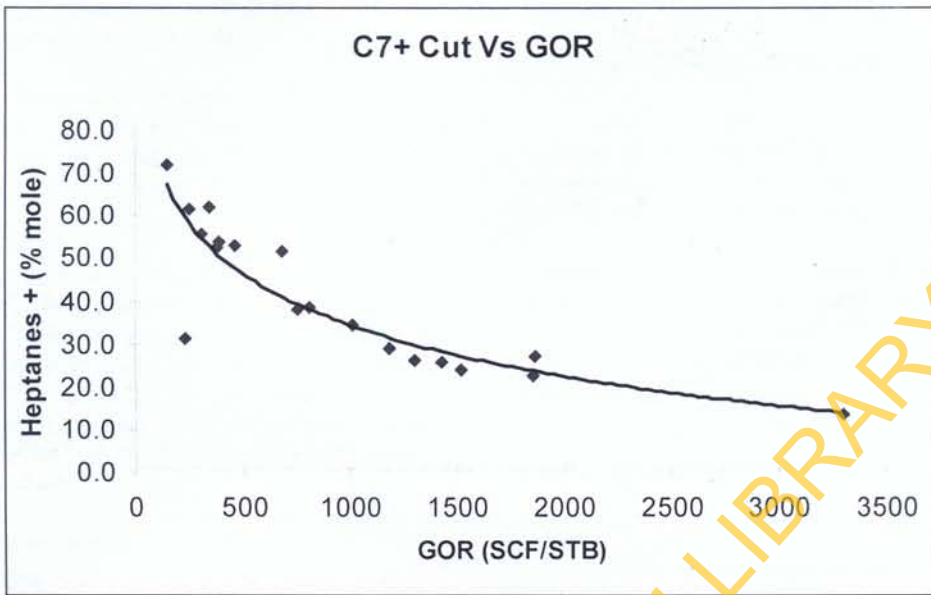


Figure 3: Heptanes plus cut Vs GOR in the Niger Delta

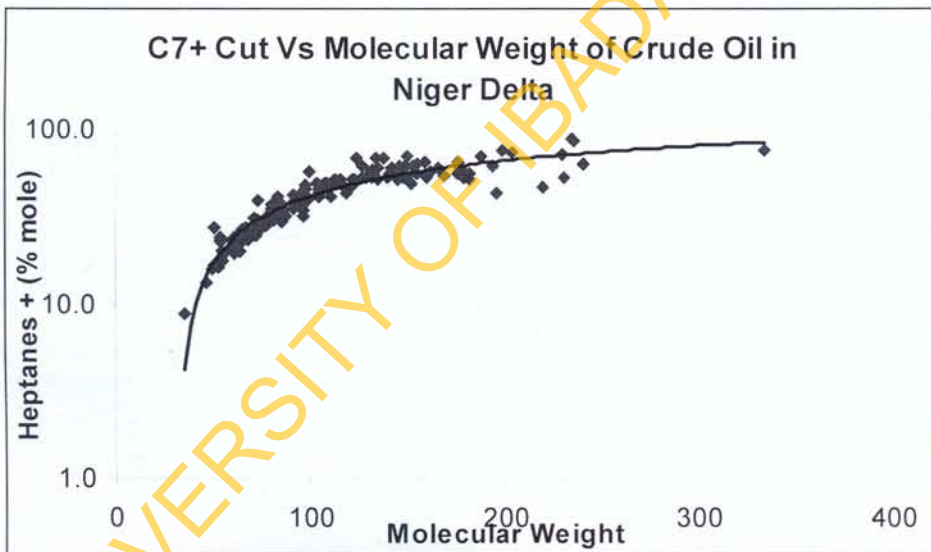


Figure 4: Heptanes Plus Cut Vs Molecular weight in the Niger Delta