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Chapter 6: FLUID CHARACTERISATION

Danesh, Ali. *PVT and phase behaviour of petroleum reservoir fluids*. Elsevier, 1998.

https://mnlotfollahi.profile.semnan.ac.ir/#about me

mnlotfollahi@yahoo.com

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Real reservoir fluids, however, could be composed of thousands of components which pose two major restrictions:

- (1) A full description of the fluid by identifying all its constituents may not be possible.
- (2) Phase behaviour calculations for systems defined by a large number of components are time consuming and particularly impractical in compositional reservoir simulation.
- A reservoir oil or condensate is commonly described by discrete hydrocarbon components up to C 6 and the non hydrocarbon gases, such as N 2, CO 2, H2S and hydrocarbon groups for heavier fractions.

The oil composition can be determined by gas chromatography, or more commonly by distillation [2] and reported as liquid fractions. The heaviest fraction, which forms the residue in distillation, can be analysed by liquid chromatography techniques [3].

Distillation

The liquid phase is generally characterised by fractional distillation and measuring the properties of the collected fractions. The distillation is commonly conducted using a column with 15

۲

theoretical equilibrium stages at a reflux ratio of 5 and is known as the *true boiling point* (TBP) distillation. The standard method is fully described in ASTM 2892-84 [2].

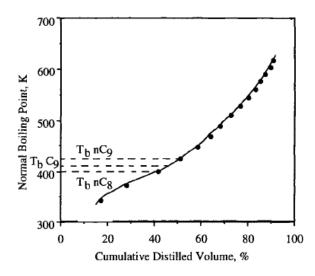
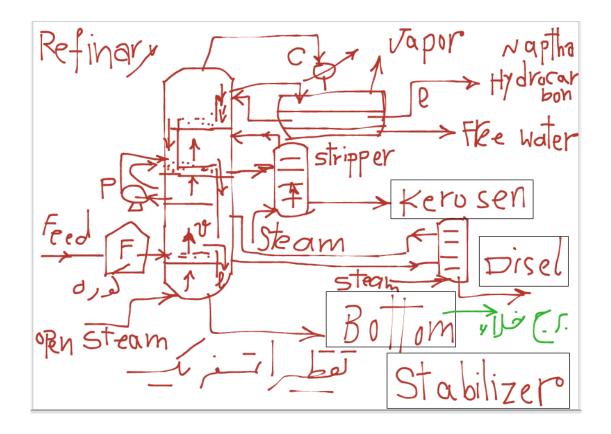


Figure 6.1. True boiling point (TBP) distillation curve of a North Sea condensate sample.



Chapter 6: FLUID CHARACTERISATION



LT/RDS-900/SA

Semi-automatic instrument for distillation composed by:

• Structure fully made in stainless steel

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- Front panel including manual controls for heating power, fan activation and main power supply
- Plate supported by a base whose height is adjustable with an elevation mechanism controlled by an external knob
- Controlled by a digital thermoregulator with PT100 A class temperature sensor
- PID range from ambient to +450°C, resolution 0,1°C
- 3 programmable set points for Gasoline, Kerosene, Gasoil for semiautomatic operation mode
- Infrared heaters 1300 Watt with ceramic-glass plate support
- Fire extinguisher system composed by:
 - solenoid valve
 - red emergency push button
 - dedicated line internally placed with holes for the emission of the fire extinguisher product with joint for the external conection
- Wide toughed glass squared window and stainless steel cover with hole for flask neck
- Cooling fan manually activated for cooling down the glass after analysis
- Refrigerated condensing unit fully made in stainless steel with double chamber insulation:
 - condensing tube made in stainless steel
 - insulated cover with handle and hole for accommodation of the thermometer with relevant support and liquid level indicator
 - integrated cooling system granting temperature from 0 to +60°C

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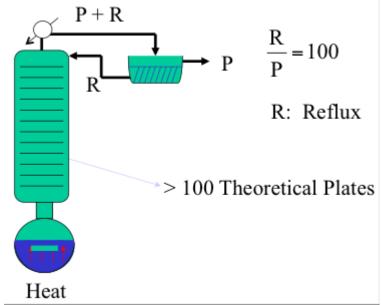
Chapter 6: FLUID CHARACTERISATION

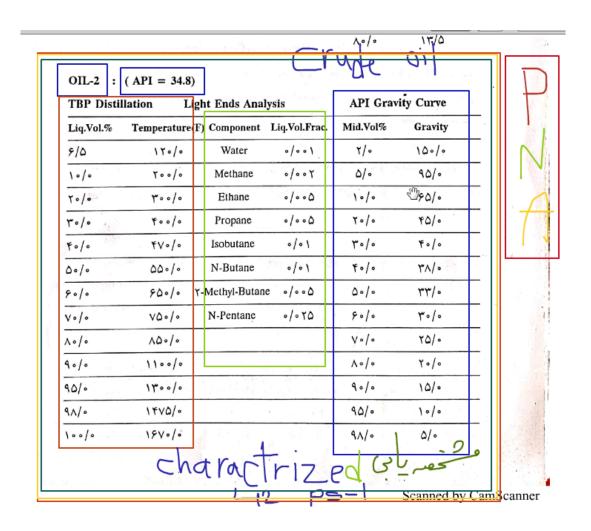
- controlled by a digital thermoregulator with PT100 A class temperature sensor with resolution 0,1°C, stirrer motor grant homogeneity/uniformity
- rear connection for coolants circulation, over flow tube and atmospheric drain cock
- white background panel for easier reading of the receiver glass cylinder level mark



Fully automatic crude oil distillation system, processor controlled

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The liquid phase contains many components with properties varying in small increments. Hence, the fractionation of liquid into pure compounds is unfeasible. Each collected fraction comprises a large number of components with close boiling points. Fractions are commonly collected within the temperature range of two consecutive normal alkanes, where each cut begins and ends at the boiling point of normal Cn-1 and normal Cn, respectively, and is referred to by the carbon number n. For example, the reported C9 fraction, nonanes, comprises all the compounds collected as distillate, within the temperature range of normal octane and normal nonane boiling points, as shown in Figure 6.1.

The fractions are called, hence, single carbon number (SCN) groups. In practice the boundaries are selected about 0.3- 0.7 oC, depending on the distillation unit and the fraction, above the normal alkane boiling points, mainly to counteract the liquid hold-up in the apparatus for improved purity.

The purity of SCN groups can further be improved by using a more efficient distillation apparatus. The use of a 90 theoretical equilibrium plate unit, instead of the standard ASTM 15 plate unit, is gaining popularity. Even then, 5-30% of the Cn fraction could be lighter than the normal Cn-1 [5].

Each cut is characterised by its molecular weight, density and normal boiling point. The boiling point is taken at its midvolume, Figure 6.1.

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The overall characteristic of hydrocarbon fractions, is commonly described by the Watson or UOP (Universal Oil Products) characterisation factor, $K_{\mathbf{w}}$, as follows:

$$K_{w} \equiv (1.8T_{b})^{\frac{1}{2}}/S \tag{6.2}$$

where Tb is the boiling point in K and S is the specific gravity.

For pure hydrocarbons the above definition of characterisation factor results in:

$$12.5 < K_w \le 13.5$$

Paraffins

6.1. Experimental Methods

$$11.0 < K_w \le 12.5$$

 $8.5 < K_w \le 11.0$

Naphthenes Aromatics

The characterisation factors of generalised SCN groups are given in Table 6.1.

Table 6.1.

Average normal boiling point, specific gravity, molecular weight and Watson characterisation factor of single carbon number groups [9].

SCN	Boiling Point	Specific Gravity	Molecular Weight	Watson Char. Fact
	к	rel. dens. at 288K	kg/kgmol	
C6	337	0.690	84	12.27
C7	366	0.727	96	11.97
C8	390	0.749	107	11.87
C9	416	0.768	121	11.82
C10	439	0.782	134	11.82
C11	461	0.793	147	11.85
C12	482	0.804	161	11.86
C13	501	0.815	175	11.85
C14	520	0.826	190	11.84
C15	539	0.836	206	11.84
C16	557	0.843	222	11.87
C17	573	0.851	237	11.87
C18	586	0.856	251	11.89
C19	598	0.861	263	11.90
C20	612	0.866	275	11.93
C21	624	0.871	291	11.93
C22	637	0.876	300	11.95
C23	648	0.881	312	11.95
C24	659	0.885	324	11.96
C25	671	0.888	337	11.99
C26	681	0.892	349	12.00
C27	691	0.896	360	12.00
C28	701	0.899	372	12.02
C29	709	0.902	382	12.03
C30	719	0.905	394	12.04
C31	728	0.909	404	12.04
C32	737	0.912	415	12.05
C33	745	0.915	426	12.05
C34	753	0.917	437	12.07
C35	760	0.920	445	12.07
C36	768	0.922	456	12.08
C37	774	0.925	464	12.07
C38	782	0.927	475	12.09
C39	788	0.929	484	12.09
C40	796	0.931	495	12.11
C41	801	0.933	502	12.11
C42	807	0.934	512	12.13
C43	813	0.936	521	12.13
C44	821	0.938	531	12.14
C45	826	0.940	539	12.14

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Table 6.2.

Paraffins, naphthenes and aromatics content of single carbon number groups of C₆ to C₉ of a typical North Sea oil [11].

Component	Weight %	Mole %	Volume %	Mol W.	Dens. g/cm ³
Hexane Group Paraffins	0.647	1.886	0.836	86.2	0.663
Hexane Group Naphthenes	0.052	0.185	0.059	70.1	0.750
Heptane Group Paraffins	0.713	1.787	0.889	100.2	0.686
Heptane Group Naphthenes	0.930	2.682	1.034	87.1	0.769
Heptane Group Aromatics	0.355	1.140	0.343	78.1	0.884
Octane Group Paraffins	0.870	1.912	1.054	114.2	0.707
Octane Group Naphthenes	1.404	3.435	1.556	102.6	0.772
Octane Group Aromatics	0.958	2.610	0.941	92.1	0.871
Nonane Group Paraffins	0.739	1.446	0.877	128.3	0.721
Nonane Group Naphthenes	0.646	1.331	0.699	122.0	0.792
Nonane Group Aromatics	1.042	2.464	1.022	106.2	0.872

The Watson characterisation factor can be related to properties other than the boiling point and specific gravity, using correlations given in Section 6.2. For example, it can be related to the molecular weight (M) and specific gravity (S) [9], using the Riazi-Daubert correlation, Eq.(6.4),

$$K_w = 4.5579 \,\mathrm{M}^{0.15178} \mathrm{S}^{-0.84573}$$
 (6.4)

The above relation is particularly useful for the last fraction, referred to as the plus fraction, where its boiling point is not known. The above equation becomes less reliable at M>300.

Gas Chromatography

The sample is injected into a heated zone, vaporised, and transported by a carrier gas, usually helium, into a column packed or internally coated with a stationary liquid or solid phase, resulting in partitioning of the injected sample constituents. General purpose columns partition components mostly according to their boiling points, hence compounds are eluted in a similar order as in distillation. The eluted compounds are carried, by the carrier gas, into a detector where the component concentration is related to the area under the detector response-time curve as shown in Figure 6.3. Individual peaks may be identified by comparing their retention times inside the column with those of known compounds previously analysed at the same GC conditions.

The two most commonly used detectors are the flame ionisation detector (FID) and the thermal conductivity detector (TCD). The HD response is almost proportional to the mass concentration of the ionised compound. It, however, cannot detect non-hydrocarbons such as N 2 and CO 2. Hence, TCD is often used for analysis of gaseous mixtures that contain nonhydrocarbon components.

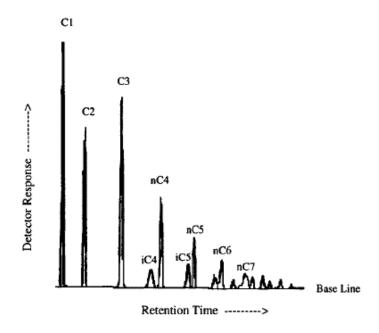


Figure 6.3. Gas chromatogram of a gas sample, using a packed column.

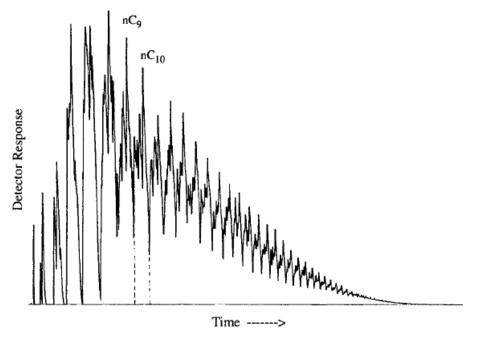


Figure 6.4. Gas chromatogram of a North Sea oil sample, using a packed column.

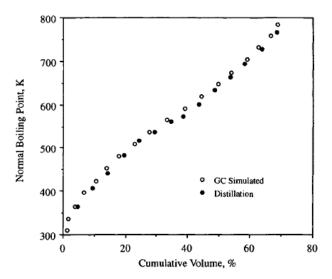


Figure 6.5. Comparison of TBP distillation curve and simulated distillation result, using gas chromatography, of an oil sample.

Table 6.4.

Comparison of single carbon number group properties measured by distillation and capillary GC analysis.

		Distillation			GC	
SCN	Weight %	Mol. W.	Dens., kg/m ³	Weight %	Mol. W.	Dens., kg/m ³
5	0.886	65	621	0.792	63	597
6	0.737	82	695	0.699	85	669
7	2.371	91	751	2.000	89	754
8	2.825	103	778	3.237	102	779
9	2.539	116	793	2.429	116	799
10+	90.642	306	869	90.846	300	868
10	2.479	132	798	2.437	134	801
11	1.916	147	803	2.191	148	803
12	2.352	163	817	2.523	162	812
13	2.091	175	836	3.106	175	827
14	3.667	190	843	3.124	190	840
15	3.722	205	849	3.984	205	845
16	2.034	215	863	3,383	218	851
17	4.135	237	844	4.244	235	842
18	3.772	251	846	3.201	250	845
19	3.407	262	857	3.523	261	854
20+	61.057	426	885	59.130	422	888

6.2 CRITICAL PROPERTIES

The critical temperature, T c, pressure, Pc, volume, v c, compressibility factor, Z c, and the acentric factor, co, of single carbon number groups and the last (plus) fraction of reservoir fluids, similar to those of discrete components, are required for phase behaviour modelling using EOS. These properties are determined from generalised correlations in terms of the specific gravity, S, boiling point, Tb, or the molecular weight, M, of single carbon groups.

Lee-Kesler Correlations [20,21]

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Lee-Kesler Correlations [20,21]

$$T_c = 189.8 + 450.6S + (0.4244 + 0.1174S)T_b + (0.1441 - 1.0069S) \times 10^5 / T_b$$
 (6.7)

$$ln P_c = 3.3864 - 0.0566/S - (0.43639 + 4.1216/S + 0.21343/S^2) \times 10^{-3} T_b
+ (0.47579 + 1.182/S + 0.15302/S^2) \times 10^{-6} T_b^2 - (2.4505 + 9.9099/S^2) \times 10^{-10} T_b^3$$
(6.8)

$$\omega = \left(\ln P_{br} - 5.92714 + 6.09648 / T_{br} + 1.28862 \ln T_{br} - 0.169347 T_{br}^{6}\right) /$$

$$\left(15.2518 - 15.6875 / T_{br} - 13.4721 \ln T_{br} + 0.43577 T_{br}^{6}\right) \text{ for } T_{br} \le 0.8$$

$$(6.9)$$

$$\omega = -7.904 + 0.1352 K_w - 0.007465 K_w^2 + 8.359 T_{br} + (1.408 - 0.01063 K_w) / T_{br} \qquad \text{for } T_{br} > 0.8$$
(6.10)

where $P_{br}=P_b/P_c$, $T_{br}=T_b/T_c$, P_b is the pressure at which T_b is measured, e.g. the normal boiling point at 0.1013 MPa (1 atmosphere) and K_w is the Watson characterisation factor, Eq.(6.2). The estimated acentric factors by the above two correlations at $T_{br}=0.8$ differ about 2%.

The acentric factor correlation, Eq.(6.9) is simply a re-arrangement of the Lee-Kesler vapour pressure correlation, Eq.(1.10).

The correlations of **Cavett** [22], given in Appendix B, for T_c and P_c are also often used in phase behaviour modelling of hydrocarbon systems. The **Edmister** correlation [23] for the acentric factor is commonly used with the Cavett correlation,

$$\omega = \left\{ \frac{3}{7} \left[\log(P_c / P_a) \right] / \left[(T_c / T_b) - 1 \right] \right\} - 1$$
(6.11)

Riazi-Daubert Correlations

Riazi and Daubert [24] developed a simple two parameter equation for predicting physical properties of hydrocarbon mixtures.

$$\theta = a \theta_1^b \theta_2^C \tag{6.14}$$

where θ is the property to be determined, and θ_1 and θ_2 can be any two parameters characterising molecular forces and molecular sizes of a component. Any pair such as (T_b, M) or (T_b, S) may be used for θ_1 and θ_2 . Properties such as the molecular weight, refractive index, critical properties, density, heat of vaporisation and thermal conductivity were successfully correlated by the above equation [24].

The authors later [25] improved the correlation as,

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$$\theta = a \left[\exp(b\theta_1 + c\theta_2 + d\theta_1\theta_2) \right] \theta_1^e \theta_2^f$$
(6.15)

where, a to f, are constants for each property as given in Table 6.5.

Table 6.5 Constants in Eq.(6.15) for T_c, P_c, v_c, M and T_b.

θ	θ1	θ2	a	b	С	d	e	f
T _c	Tb	S	9.5233E+00	- 9.3140E-04	- 0.54444	6.4791E-04	0.81067	0.53691
T_c	M	S	3.0800E+02	- 1.3478E-04	- 0.61641	0.0000E+00	0.2998	1.0555
P_c	T_b	S	3.1958E+04	- 8.5050E-03	- 4.8014	5.7490E-03	- 0.4844	4.0846
P_c	M	S	3.1166E+02	- 1.8078E-03	- 0.3084	0.0000E+00	- 0.8063	1.6015
(v_c/M)	T_b	S	6.0490E-05	- 2.6422E-03	- 0.26404	1.9710E-03	0.7506	- 1.2028
(v_c/M)	M	S	7.5288E-04	- 2.6570E-03	0.5287	2.6012E-03	0.20378	- 1.3036
M	T_b	S	1.0321E+03	9.7754E-04	- 9.53384	1.9990E-03	0.97476	6.51274
Тb	M	S	3.7659E+00	3.7741E-03	2.984036	- 4.2529E-03	0.401673	- 1.58262

(70 < M < 300 300 < T_b < 610 K)

Table 6.6. Comparison of several methods for prediction of critical properties.

Method	% Dev. Critical	Temperature	% Dev. Critical Pressure		
	Abs. Average	Maximum	Abs. Average	Maximum	
Riazi-Daubert	0.5	2.2	2.7	13.2	
Twu	0.6	2.4	3.9	16.5	
Kesler-Lee	0.7	3.2	4.0	12.4	
Cavett	3.0	5.9	5.5	31.2	

Perturbation Expansion Correlations

Perturbation Expansion Correlations

These methods initially correlate the properties of normal paraffins as the reference, and then extend these correlations to petroleum fractions. The correlations developed by Twu [26], who used the difference between the specific gravity of the hydrocarbon fraction and that of the normal paraffin with the same boiling point as the correlating parameter are as follows.

Normal Paraffins

The properties of normal paraffins are correlated with the normal boiling point temperature,

$$\begin{split} T_{cp} &= T_b \Big[0.533272 + 0.343831 \big(10^{-3} \big) T_b + 2.526167 \big(10^{-7} \big) T_b^2 \\ &- 1.65848 \big(10^{-10} \big) T_b^3 + 0.0460774 / \big(T_b / 100 \big)^{13} \Big]^{-1} \end{split} \tag{6.16}$$

$$P_{cp} = (0.318317 + 0.099334\psi^{\frac{1}{2}} + 2.89698\psi + 3.00546\psi^{2} + 8.65163\psi^{4})^{2}$$
(6.17)

$$v_{cp} = \left[0.82055 + 0.715468\psi + 2.21266\psi^{3} + 13411.1\psi^{14}\right]^{-8}$$
(6.18)

$$S_p = 0.843593 - 0.128624\psi - 3.36159\psi^3 - 13749.5\psi^{12}$$
(6.19)

where the subscript p refers to properties of normal paraffins and,

$$\psi = 1 - T_b / T_{co} \tag{6.20}$$

The molecular weight of paraffins is given by the following implicit relation,

$$T_{b} = \exp\left[\left(5.12640 + 2.71579 \ln M_{p} - 0.286590 \left(\ln M_{p}\right)^{2} - 39.8544 / \left(\ln M_{p}\right) - 0.122488 / \left(\ln M_{p}\right)^{2}\right] - 13.7512 \ln M_{p} + 19.6197 \left(\ln M_{p}\right)^{2}$$
(6.21)

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which can be solved iteratively using the following initial guess,

$$M_p = T_b / (5.800 - 0.0052T_b) \tag{6.22}$$

Petroleum Fractions

The properties of any petroleum fraction are estimated by adjusting the calculated properties of the normal paraffin with the same boiling point as follows:

Critical Temperature:

$$T_{c} = T_{cp} \left[(1 + 2f_{T}) / (1 - 2f_{T}) \right]^{2}$$

$$f_{T} = \Delta S_{T} \left[-0.270159 / T_{b}^{\frac{1}{2}} + \left(0.0398285 - 0.706691 / T_{b}^{\frac{1}{2}} \right) \Delta S_{T} \right]$$
(6.23)

$$\Delta S_{T} = \exp[5(S_{p} - S)] - 1$$

Critical Volume:

$$v_{c} = v_{cp} [(1 + 2f_{v})/(1 - 2f_{v})]^{2}$$

$$f_{v} = \Delta S_{v} [0.347776/T_{b}^{\frac{1}{2}} + (-0.182421 + 2.24890/T_{b}^{\frac{1}{2}})\Delta S_{v}]$$

$$\Delta S_{v} = \exp[4(S_{p}^{2} - S^{2})] - 1$$
(6.24)

Critical Pressure:

$$P_{c} = P_{cp} \left(T_{c} / T_{cp} \right) \left(v_{cp} / v_{c} \right) \left[\left(1 + 2f_{p} \right) / \left(1 - 2f_{p} \right) \right]^{2}$$

$$f_{p} = \Delta S_{p} \left[\left(2.53262 - 34.4321 / T_{b}^{\frac{1}{2}} - 0.00230193T_{b} \right) + \left(-11.4277 + 187.934 / T_{b}^{\frac{1}{2}} + 0.00414963T_{b} \right) \Delta S_{p} \right]$$
(6.25)

$$\Delta S_p = \exp [0.5(S_p - S)] - 1$$

Molecular Weight:

$$\ln M = (\ln M_p)[(1 + 2f_M)/(1 - 2f_M)]^2$$

$$f_M = \Delta S_M [|\Psi| + (-0.0175691 + 0.143979/T_b^{\frac{1}{2}})\Delta S_M]$$

$$\Psi = 0.0123420 - 0.244541/T_b^{\frac{1}{2}}$$

$$\Delta S_M = \exp[5(S_p - S)] - 1$$
(6.26)

The above method, because of its reliability, has been used to calculate the critical properties of generalised SCN groups, using the reported boiling point and specific gravity in Table 6.1, with the results given in Table A.2 in Appendix A.

Riazi and Daubert [25] compared predictions of their correlation, Eq.(6.15) using T_b and S, with others for 138 pure compounds, with the results given in Table 6.6.

Table 6.6.
Comparison of several methods for prediction of critical properties.

Method	% Dev. Critica	l Temperature	% Dev. Critica	Dev. Critical Pressure	
	Abs. Average	Maximum	Abs. Average	Maximum	
Riazi-Daubert	0.5	2.2	2.7	13.2	
Twu	0.6	2.4	3.9	16.5	
Kesler-Lee	0.7	3.2	4.0	12.4	
Cavett	3.0	5.9	5.5	31.2	

Example 6.1.

Calculate the critical temperature, pressure, volume and the acentric factor for C₁₄ with properties as reported in the generalised property table, Table 6.1, using the methods of Twu (Lee-Kesler for the acentric factor) and Riazi-Daubert (Edmister for the acentric factor).

Solution:

The specific gravity, boiling point and molecular weight of C_{14} are read as 0.826, 520 K and 190 kg/kgmol, respectively, from Table 6.1.

Twu Correlations

The properties of the normal alkane with the same boiling point as that of C_{14} , that is 520 K, are initially calculated as follows:

***************************************	T _b , K	T _{cp} , K	1-T _b /T _{cp}	P _{cp} , MPa	V _{cp}	Sp
Equation	Table A.2	6.16	6.20	6.17	6.18	6.19
	520	686.8	0.2429	1.6348	0.8135	0.7635

Next, the above calculated normal alkane properties are adjusted, based on the difference between the C_{14} specific gravity, 0.826, and that of the normal alkane calculated above, 0.7635.

***************************************	ΔS_{τ}	f _T	T _c , K	ΔS_v	f,	v _c , m³/kgmol	ΔS_p	f_p	P _e , MPa
Equation			6.23			6.24			6.25
	-0.2681	0.003812	708	-0.3276	-0.01399	0.727	-0.03073	0.004386	1.953

As the reduced boiling point temperature is equal to 520/708=0.734, Eq.(6.9) of the Lee-Kesler method is used to calculate the acentric factor, which results in,

 $\omega = 0.536$

The calculated values for single carbon number groups, C₆-C₄₅, using the above method, are given in Table A.2 in Appendix A.

Riazi-Daubert Correlations

The critical properties can be estimated by either using measured T_b -S, or M-S data of C_{14} . The results of both approaches, using Eq.(6.15), are given in the following table.

	T _c ,	K	v _c m ³ /	kgmol	P _e , MPa	
Data used	T _b , S	M, S	T _b , S	M, S	T _b , S	M, S
	710	711	0.750	0.751	1.902	1.835

The measured values of specific gravity and boiling point, as the most readily available data, are commonly used to estimate the critical properties.

Using the Edmister correlation, Eq.(6.11), along with the above calculated T_c and P_c , results in,

 $\omega = 0.486$

Single Carbon Number Function

A simple, but very useful, approach is to use a function to describe the concentration of SCN groups. Various functional forms have been suggested and applied [28-30], with reasonable success. The simplest of all is, that of Katz [28] for the C₇₊ fraction of condensate systems, as expressed mathematically [19] by,

$$z_{C_n} = 1.38205 z_{C_{7_n}} \exp(-0.25903n)$$
(6.27)

where z_{C_n} is the mole fraction of single carbon number group C_n .

A linear relation between the SCN and logarithm of concentration is generally adequate to describe heavy fractions of most reservoir fluids,

$$\ln z_{C_n} = A + Bn \tag{6.28}$$

where A and B are constants for each fluid. Pedersen et al. [31] proposed the above equation, and evaluated it for a large number of North Sea reservoir fluids with measured compositional analysis to C_{80+} . The above simple expression was capable of representing the measured data so well that the authors did not see any advantage in having measured compositional analysis beyond C_{20+} in preference to calculated data from Eq.(6.28).

Continuous Description

The above approach of describing the concentration of SCN groups by a function, may appear as a continuous description of the fluid, but it is basically a discrete representation. The function describes the heavy part by a number of SCN groups, and is only valid at the discrete

carbon numbers. In mathematical terms, the function provides the value of concentration integral between C_{n-1} and C_n ,

$$z_{C_n} = \int_{C_{n-1}}^{C_n} dz_i \tag{6.34}$$

where i refers to all the components comprising the SCN group n.

A more appropriate approach is the continuous description of the fluid, where the distribution of all its constituents, instead of carbon groups, is aimed. Indeed the carbon groups reported by laboratories are determined by integration of compounds comprising the groups. For example, the area under the curve in Figure 6.4 between nC_9 and nC_{10} is taken as the concentration of C_{10} group.

The continuous description reflects the true nature of reservoir fluids that are composed of many compounds, with properties varying so gradually that do not allow distinctive identification.

The continuous distribution of components can be expressed by a function, F(I), such that,

$$\int F(I)dI = z \tag{6.35}$$

where z is the total concentration of all the components, represented by I, within the integral boundaries. If all the components of a fluid is described by the continuous description, then,

$$\int_{I} \mathbf{F}(\mathbf{I}) d\mathbf{I} = 1 \tag{6.36}$$

In the more practical semi-continuous description, only the heavy part (say > C_7) is described by the continuous function,

$$\int_{\Gamma} F(I)dI = z_{D} \tag{6.37}$$