

A Continuous Model for C₇₊ Fraction Characterization of Petroleum Fluids

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In this paper, based on a two-parameter distribution model, a method is presented to predict complete property distributions for molecular weight, boiling point, specific gravity, and refractive index of a C₇₊ fraction. Only three mixture bulk properties such as molecular weight, specific gravity, and refractive index are needed for this technique. If a distillation (TBP) analysis for the fraction is available, then only two bulk properties such as molecular weight and specific gravity (or refractive index) are sufficient. Predicted distributions for various properties are compared with experimental data of some 48 crude samples. The method is also applied for flash vaporization of a Russian crude oil, and predicted distributions for feed, vapor, and liquid streams are compared with actual data. Splitting and lumping schemes of petroleum fractions using the proposed distribution model are also presented by two different approaches with detailed computational procedures.

Introduction

Characterization of crude oil is an important step in the application of equations of state for pressure–volume–temperature (PVT) predictions and phase behavior calculations. Such calculations are needed in reservoir simulation or in the design and operation of refinery distillation columns. An insufficient description of heavier hydrocarbons (e.g., heptanes and heavier; C₇₊) reduces the accuracy of PVT predictions as shown by Whitson (1983). Volumetric and phase behaviors of even volatile oil and gas–condensate samples are quite sensitive to properties of the heavier components. In the determination of properties of a C₇₊ fraction, usually distributions of some basic properties such as molecular weight, true boiling point (TBP), and specific gravity (or density) are needed. Application of continuous distribution models in the prediction of the phase behavior of heavy reservoir fluids is also demonstrated by Kawanada et al. (1991). Whitson (1983, 1984) used a gamma distribution model to describe molecular weight/mole fraction relations for C₇₊ fractions. Another widely used distribution model is the exponential function as discussed by Ahmed (1989). Gamma distribution model is a three-parameter function while the exponential function is a two-parameter model. In addition, the gamma and exponential models are mainly used for the molecular weight distribution of plus fractions. A method based on a constant Watson *K* factor is outlined by Soreide (1989) and Whitson (1984) to generate the distribution of specific gravity. When the distribution model is known, then a lumped fraction can be split into several pseudocompounds or single carbon number (SCN) groups with known mole fractions by using mathematical techniques such as the Gaussian quadrature method (Stroud and Secrest, 1966). Soreide (1989) has shown the application of the Gaussian quadrature method in obtaining appropriate pseudocomponents for a C₇₊ fraction using the gamma distribution model. Once pseudocomponents are determined, then correlations such as Riazi and Daubert (1980) or Riazi and Al-Sahhaf (1996) can be used to estimate various properties of a C₇₊ fraction (Ahmed, 1989).

Unfortunately, complete experimental data on the distribution of molecular weight, TBP, and density for a hydrocarbon-plus fraction are seldom available. Usually bulk properties such as molecular weight, specific gravity, density, or refractive index are available. In some cases only complete TBP analysis may be available for a hydrocarbon-plus fraction. The main purpose of this paper was to present a new method that can be used to predict complete distributions for various properties of a C₇₊ fraction based on the knowledge of a mixture's bulk properties which are easily measurable. Another objective of this work was to develop splitting and lumping schemes of petroleum fractions based on the proposed distribution model.

Two-Parameter Distribution Model

Riazi (1989) developed a simple and versatile distribution model for various properties of a hydrocarbon-plus fraction in the following form:

$$P^* = \left[\frac{A}{B} \ln \left(\frac{1}{x^*} \right) \right]^{1/B} \quad (1)$$

where $P^* = (P - P_0)/P_0$ and $x^* = 1 - x$ in which x is the cumulative weight, mole, or volume fraction and P is a property such as absolute boiling point (T_b), molecular weight (M), specific gravity (S), density (d), or refractive index parameter (I). Parameter I is related to the refractive index (n) at 20 °C by the equation:

$$I = \frac{n^2 - 1}{n^2 + 2} \quad (2)$$

P_0 is the parameter specific for each property (T_0 , M_0 , S_0 , I_0) and each sample. A is also a parameter specific for each property (A_T , A_M , A_S , A_I) and each sample. B is a parameter specific for each property (B_T , B_M , B_S , B_I) but is the same for all samples. It was determined that for most samples examined $B_S = B_I = 3$, $B_M = 1$, and $B_T = 1.5$. In eq 1, for specific gravity (S), density (d), and refractive index parameter (I), x is the cumulative volume or weight fraction, while for molecular weight (M), x is the cumulative mole fraction.

With values of B known for different properties, eq 1 becomes a two-parameter distribution model where P_0

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and A should be determined. As discussed by Riazi (1989), because eq 1 well represents fractions containing heavy components and it is applicable to all various parameters (M , T_b , S , I , d) with only two parameters to be determined, it is an appropriate model to be used in this study. Equation 1 can be converted into a linear form:

$$Y = C_1 + C_2 X \quad (3)$$

where: $Y = \ln P^*$, $X = \ln \ln(1/x^*)$, $B = 1/C_2$, and $A = B \exp(C_1 B)$. P_0 and A can be determined by linear regression of data through eq 3. The probability density function $F(P^*)$ deduced from eq 1 is in the following form:

$$F(P^*) = \frac{B^2}{A} P^{*B-1} \exp\left(-\frac{B}{A} P^{*B}\right) \quad (4)$$

This equation can also be written in terms of property, P , if P^* is replaced by its definition. Average mixture properties calculated from eq 1 (or eq 4) in terms of P^* are given by

$$P_{av}^* = \int_0^\infty P^* F(P^*) dP^* = \left(\frac{A}{B}\right)^{1/B} \Gamma\left(1 + \frac{1}{B}\right) \quad (5)$$

where Γ is the gamma function. Equation 5 can be applied to M , T_b , S , and I . For S and I , distributions must be in cumulative volume or weight fractions. However, as is discussed by Riazi (1989), if S is given in terms of cumulative weight fraction, then S_{av}^* is calculated by the relation

$$S_{av}^* = \int_0^\infty F(S^*) \frac{dS^*}{S^* + 1} \quad (6)$$

If fixed values for parameter B are used for different properties, then eq 5 gives the following relations for the average properties:

$$M_{av}^* = A_M \quad (7)$$

$$T_{av}^* = 0.689 A_T^{2/3} \quad (8)$$

$$I_{av}^* = 0.619 A_I^{1/3} \quad (9)$$

Once P_{av}^* has been determined, the average property P_{av} for the mixture can be obtained from the relation

$$P_{av} = P_0(1 + P_{av}^*) \quad (10)$$

For the specific gravity, S , when it is represented in terms of cumulative weight fraction, then the average value is calculated from the following relations:

if $A_S > 0.05$

$$S_{av} = S_0(1.3818 + 0.3503 A_S - 0.1932 A_S^2 + 0.059 \ln A_S) \quad (11)$$

if $A_S \leq 0.05$

$$S_{av} = S_0(1.25355 + 1.44886 A_S - 5.9777 A_S^2 + 0.02951 \ln A_S) \quad (12)$$

For 48 samples of oils and condensates listed in Table 1, complete data on distributions of M , T_b , S , and n versus mole or weight fractions were available. Mixture

Table 1. Bulk Properties for C_{7+} Samples Used in This Study

sample	data source ^a	fluid residue type ^b	M_{7+}	S_{7+}	n_{7+}
1	a	BO	142.8	0.7717	1.4274
2	a	BO	193.3	0.7995	1.4345
3	b	BO	289.4	0.9041	1.5194
4	b	BO	206.2	0.8505	1.4512
5	b	BO	348.2	0.9386	1.5057
6	c	BO	177.5	0.8067	1.4472
7	d	BO	227.5	0.8518	1.4752
8	e	BO	257.2	0.8732	1.4584
9	e	BO	205.7	0.8412	1.4457
10	f	BO	256.1	0.8759	1.4962
11	g	BO	210.9	0.8451	1.4708
12	g	BO	217.1	0.8449	1.4723
13	g	BO	236.2	0.8525	1.4814
14	g	BO	232.0	0.8658	1.4839
15	h	BO	230.3	0.8650	1.4836
16	h	BO	213.6	0.8458	1.4694
17	h	GC	149.4	0.8195	1.4594
18	h	GC	120.2	0.7955	1.4440
19	h	GC	118.9	0.7597	1.4234
20	i	GC	149.9	0.8165	1.4595
21	i	GC	150.5	0.8162	1.4813
22	i	GC	155.4	0.8086	1.4497
23	j	GC	129.1	0.7865	1.4387
24	j	BO	214.0	0.8598	1.4921
25	j	GC	170.6	0.8005	1.4451
26	j	GC	169.2	0.8008	1.4981
27	j	GC	153.7	0.7871	1.4281
28	j	GC	176.5	0.8043	1.4334
29	j	GC	175.2	0.8033	1.4470
30	j	BO	216.7	0.8517	1.4526
31	j	BO	232.9	0.8534	1.4769
32	j	BO	242.9	0.8833	1.4980
33	j	BO	211.4	0.8458	1.4694
34	j	BO	211.2	0.8459	1.4714
35	j	BO	247.9	0.8839	1.4946
36	j	BO	221.5	0.8338	1.4625
37	j	GC	125.3	0.7737	1.4302
38	j	GC	132.1	0.8039	1.4469
39	j	GC	128.4	0.7909	1.4401
40	j	BO	267.8	0.9033	1.4735
41	j	GC	172.0	0.8127	1.4544
42	j	GC	151.6	0.7917	1.4400
43	j	GC	122.5	0.7633	1.4250
44	j	GC	140.1	0.8068	1.4358
45	j	GC	170.5	0.8113	1.4537
46	j	GC	175.2	0.8055	1.4366
47	j	GC	119.3	0.7838	1.4379
48	j	GC	163.8	0.8137	1.4573

^a References are as follows: (a) Jacoby and Berry (1959); (b) Lee et al. (1979); (c) Austad et al. (1983); (d) Hariu and Sage (1969); (e) Haaland (1981); (f) Berge (1981); (g) Pedersen et al. (1984a); (h) Pedersen et al. (1984b); (i) Pedersen et al. (1985); (j) Whitson et al. (1988). ^b BO: black oil. GC: gas condensate.

bulk properties for M , S , and n for each sample of C_{7+} are given in Table 1. When eq 1 is used to predict distributions of various properties for samples listed in Table 1, average absolute deviations (AAD) of 3 for M , 3 K for T_b , and 0.6% for both S and n were obtained for a total of 650 subfractions. The gamma distribution model predicts molecular weight and boiling point distributions with accuracy nearly the same as eq 1 while the constant Watson K method predicts specific gravity distributions with AAD of 1.2%. The exponential model predicts molecular weight with AAD of 4. The exponential distribution model is not suitable to represent T_b , S , and n distributions.

A comparison between various distribution models when applied to a heavy fraction (Rodgers et al., 1987) is shown in Figure 1. The mixture mole average molecular weight is 562. The estimated average molecular weight from eq 5 is 563, while from the gamma

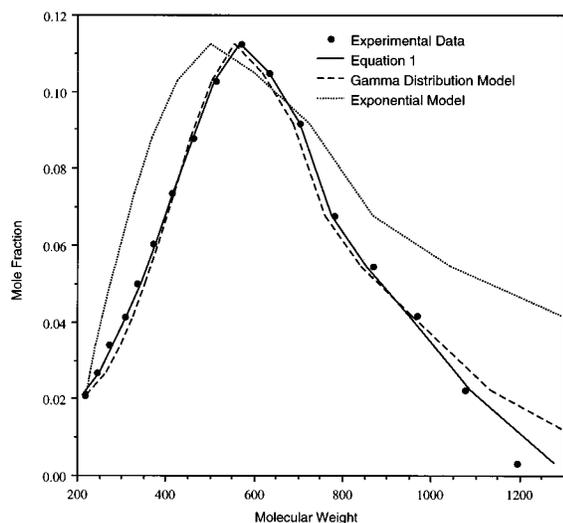


Figure 1. Comparison of various distribution models for molecular weight of a heavy petroleum mixture. Data are taken from Rodgers et al. (1987).

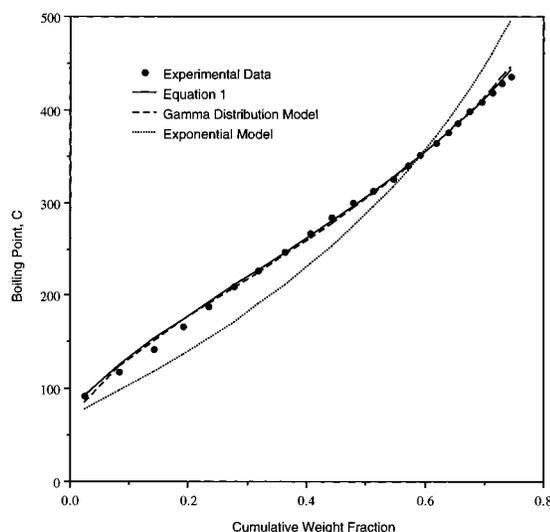


Figure 2. Comparison of various models for prediction of boiling point distribution of sample no. 16.

and exponential distribution models they are 559 and 569, respectively. Similar evaluations for boiling point and specific gravity distributions for an oil sample (no. 16) and a condensate sample (no. 19) in Table 1 are presented in Figures 2 and 3. For sample no. 19 the estimated average specific gravity from eq 5 is 0.7612 versus the experimental value of 0.7597, giving a deviation of 0.2%. The exponential model gives an average specific gravity of 0.754 with a deviation of 1.7%. These evaluations show that for very heavy fractions eq 1 predicts better distributions than the gamma distribution model especially toward the heavy end. The flexibility of the proposed model is due to the role of parameter B in the exponential part of eq 4. This is the main difference between the proposed model and the gamma distribution model. The exponential model is not appropriate for heavy fractions as shown in Figure 1. Figures 2 and 3 show that the exponential function is not suitable for presentation of boiling point and specific gravity distributions. While it seems that eq 1 is equivalent to the gamma distribution model for presentation of molecular weight and boiling point distributions, eq 1 actually is a two-parameter function because parameter B can be fixed for each property. Therefore, when parameters A and P_0 are known for a

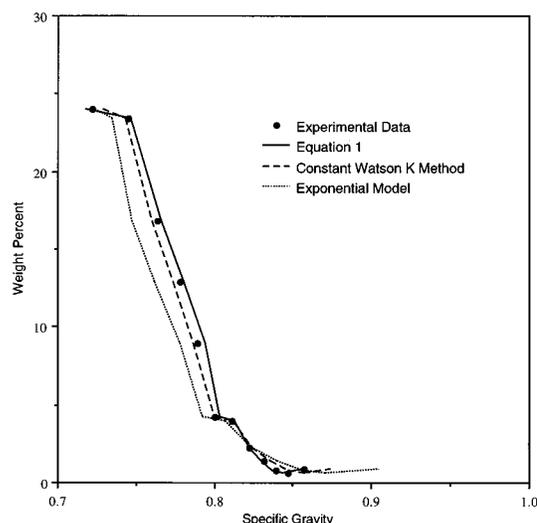


Figure 3. Comparison of various methods for prediction of specific gravity distribution of sample no. 19.

property, a complete distribution can be determined for that property.

Now, we present the methods that can generate property distributions by predicting parameters P_0 and A in eq 1 for different properties with use of only three mixture bulk properties which are readily available or measurable. These properties are molecular weight, specific gravity, and refractive index (at 20 °C) for a C_{7+} fraction such as those given in Table 1. Two methods are presented here.

Prediction of Distributions Using Bulk Properties: M , S , n (Method A)

The beauty of the distribution model given by eq 1 (or eq 4) is that only two parameters (P_0 and A) must be determined for each property in order to predict the whole distribution, since values of B are known for each property. For example, if M_0 is known, then from definition of P^* we have

$$M_{av}^* = \frac{M_{av} - M_0}{M_0} \quad (13)$$

where M_{av} is the mixture bulk molecular weight of the C_{7+} fraction which is assumed to be known from measurement. Similarly, S_{av}^* and I_{av}^* can be estimated from knowledge of S_{7+} and n_{7+} (or I_{7+}). Once M_{av}^* , S_{av}^* , and I_{av}^* are known, A_M , A_I , and A_S can be easily calculated through eqs 7, 9, and 11 (or 12). However, as mentioned before, eq 7 was obtained based on a cumulative mole fraction (x_m), while eqs 11 and 12 were derived based on a cumulative weight fraction (x_w). Once distributions for M and S are known, distributions of boiling point (T_b) can be determined using equations given by Riazi and Daubert (1987):

$$T_b = 3.76587 \exp(3.7741 \times 10^{-3}M + 2.98404S - 4.25288 \times 10^{-3}MS)M^{0.40167}S^{-1.58262} \quad (14)$$

where T_b is in degrees Kelvin. This equation, which was derived based on data for 140 pure hydrocarbons, predicts boiling points with an average absolute deviation of 1%. This equation can also be applied to narrow boiling range fractions, but it cannot be applied to crude oils or C_{7+} fractions.

Since parameters M_0 , S_0 , and I_0 are not known, at first we should guess some initial values for these parameters. For example, values of 72 for M_0 and 0.59 for S_0 can be used as the initial guesses as these are the lowest values for samples in Table 1. Fortunately, analysis of data on values of M_0 , S_0 , and I_0 for samples given in Table 1 indicates that there is a good relation among these three parameters as follows:

$$I_0 = 0.7454 \exp(-0.01151M_0 - 2.37842S_0 + 0.01225M_0S_0)M_0^{0.2949}S_0^{1.53147} \quad (15)$$

The above equation can reproduce values of I_0 with an AAD of 0.3%. However, based on properties of more than 500 pure compounds and narrow boiling range petroleum fractions, a more general relation for the prediction of parameter I was obtained in the following form:

for $M \leq 300$

$$I = 0.12399 \exp(3.4622 \times 10^{-4}M + 0.90389S - 6.0955 \times 10^{-4}MS)M^{0.02264}S^{0.22423} \quad (16)$$

for $M > 300$

$$I = 0.01102 \exp(-8.61126 \times 10^{-4}M + 3.228607S + 9.07171 \times 10^{-4}MS)M^{0.02426}S^{-2.25051} \quad (17)$$

The above equations predict refractive indices with AAD of 0.05%. Similar relations are available to estimate the refractive index from boiling point and specific gravity as given by Riazi and Daubert (1987) or the *API Technical Data Book* (1989):

for $M \leq 300$

$$I = 2.3435 \times 10^{-2} \exp(7.029 \times 10^{-4}T_b + 2.468S - 10.267 \times 10^{-4}T_bS)T_b^{0.0572}S^{-0.72} \quad (18)$$

for $M > 300$

$$I = 1.8422 \times 10^{-2} \exp(11.6352 \times 10^{-4}T_b + 5.144S - 5.92 \times 10^{-4}T_bS)T_b^{-0.4077}S^{-3.333} \quad (19)$$

In these relations T_b is in degrees Kelvin. The refractive index, n , can be estimated through eq 2 with parameter I estimated from the above relations.

Steps to predict distributions for M , T_b , S , and I (or n) from three bulk properties of C_{7+} can be summarized as follows:

1. Read values of M , S , and I for a given C_{7+} sample. If I is not available, eq 16 or 17 may be used to estimate this property.
2. Guess an initial value for M_0 (assume $M_0 = 72$) and calculate M_{av}^* from eq 13.
3. Calculate A_M from eq 7.
4. Choose 20 arbitrary cuts for the mixture with equal mole fractions of 0.05. Then calculate M for each cut from eq 1.
5. Convert mole fractions (x_m) to weight fractions (x_w) using molecular weights obtained in step 4.
6. Guess an initial value for S_0 (assume $S_0 = 0.59$).
7. Calculate A_S from eq 11 (or 12) using Newton's method.
8. Find the distribution of S in terms of cumulative weight fraction from eq 1 and calculate S for each cut.

9. Using S distribution, convert weight fractions (x_w) into volume fractions (x_v).

10. Using M and S versus cumulative weight fractions, calculate T_b for each cut from eq 14.

11. Using M and S , calculate I from eq 16 (or 17).

12. From data on I versus cumulative volume fraction (x_v), calculate parameters I_0 and A_I from eqs 1 and 3. Then calculate I_{av} from eqs 9 and 10.

13. Calculate $\epsilon_1 = |(I_{av,calc.} - I_{7+})/I_{7+}|$.

14. If $\epsilon_1 \leq 0.005$, continue from step 15. Otherwise, go back to step 6 with $S_{new} = S_{old} + 0.005$ and repeat steps 7–13.

15. Calculate I_0 from eq 15.

16. Calculate $\epsilon_2 = |(I_{0,calc.} - I_{0,step12})/I_{0,calc.}|$.

17. Go back to step 2 with a new guess for M_0 (higher than the initial guess). Repeat steps 2–17 until ϵ_2 becomes minimum and less than 0.005.

18. Using data for T_b versus cumulative weight fraction, determine parameters T_0 and A_T from eqs 1 and 3.

19. Print M_0 , A_M , S_0 , A_S , T_0 , A_T , I_0 , and A_I .

20. Generate distributions for M , S , T_b , and I using eq 1 with parameters in step 19.

Prediction of Distributions Using M , S , and TBP (Method B)

In some cases TBP (true boiling point) distribution of a sample is known through the distillation curve. For such samples only two bulk properties such as M and S or M and n are needed. For these cases, with an initial guess on S_0 , an initial distribution for S can be determined. Then using T_b and S for each subfraction, M can be estimated through the relation given by the *API Technical Data Book* (1989):

$$M = 42.9654 \exp(2.097 \times 10^{-4}T_b - 7.787S + 2.0848 \times 10^{-3}T_bS)T_b^{1.26007}S^{4.98308} \quad (20)$$

Using eq 18, parameter I and as a result its distribution can be determined. For this method the calculation procedure can be summarized as follows:

1. Read values of M and S and the TBP distribution (e.g., simulated distillation curve) for a given crude oil sample.
2. Choose 20 arbitrary cuts for the mixture with equal weight (or volume) fractions of 0.05. Then find values of boiling points at these points from the TBP curve. If simulated distillation is available, weight fraction should be used for each cut.
3. Find parameters T_0 and A_T using eq 3 and data given in step 2.
4. Guess an initial value for S_0 (assume $S_0 = 0.59$).
5. Calculate A_S from eq 11 (or 12) using Newton's method.
6. Find the distribution of S in terms of the cumulative weight fraction using eqs 1 and 2. The specific gravity can be used to convert volume fractions into weight fractions if TBP is originally available in terms of the cumulative volume fraction.
7. Using values of T_b and S for each cut, calculate M from eq 20.
8. Use values of M calculated in step 7 to convert weight fractions into mole fractions (x_m).
9. Using data calculated in step 8, find the molar distribution of molecular weight. In this step parameters M_0 and A_M are calculated from eq 3.

10. Calculate values of I from T and S for each cut using eq 18 (or 19).

11. Find values of I_0 and A_I by eq 3 using data generated in step 10.

12. Using M_0 obtained in step 9 and S_0 assumed in step 4, calculate a value for I_0 from eq 15.

13. Assume $I_1 = I_0$ calculated from step 11 and $I_2 = I_0$ calculated from step 12. Then calculate $\epsilon_1 = |(I_2 - I_1)/I_1|$.

14. If $\epsilon_1 \geq 0.005$, go back to step 4 using $S_{0,\text{new}} = S_{0,\text{old}} + 0.005$. If $\epsilon_1 < 0.005$, go to step 15.

15. Print T_0 , A_T , M_0 , A_M , S_0 , A_S , I_0 , and A_I .

16. Generate complete distributions for M , S , T_b , and I using eq 1 with parameters determined from step 15.

Splitting and Lumping Schemes

Usually detailed analytical data for reservoir fluids are available from C_1 to C_6 and for compounds heavier than C_7 ; they are grouped into a single C_{7+} fraction with known bulk properties. For such cases method A outlined above can be used to obtain distribution of various properties. Once the molar distribution is known, then C_{7+} can be splitted into a number of pseudocomponents with known mole fractions, molecular weights, and specific gravities. In many cases detailed analytical data on a reservoir fluid are available to higher carbon numbers and heavy compounds are grouped into a C_{20+} or even C_{30+} . For these cases if molecular weight and specific gravity are available versus molar composition of each SCN, then eq 1 can be conveniently applied to determine molecular weight and specific gravity distributions. But if M and S data are not available for each SCN, one may use properties of SCN groups recommended by Riazi and Al-Sahhaf (1996) or Katz and Firoozabadi (1978) to obtain complete distributions. However, for the sake of the computational efficiency, it is necessary to lump various SCN groups into a few (3, 5, or 7) pseudocomponents. In order to do so, data available on M and S distributions for SCN groups heavier than C_6 should be used to obtain distribution functions through eq 1 and then pseudocomponents can be determined from distribution functions.

Two methods are recommended in this paper to obtain these pseudocomponents. The first method is application of the Gaussian quadrature method as discussed by Stroud and Secrest (1966). The Gaussian quadrature method is used to provide a discrete representation of continuous functions using different numbers of quadrature points. The number of pseudocomponents is the same as the number of quadrature points. This method gives the following relations for calculation of properties and mole fractions of the pseudocomponents:

$$P_i = P_0 \left[1 + \left(\frac{A}{B} \right)^{1/B} y_i^{1/B} \right] \quad (21)$$

$$z_i = w_i \quad (22)$$

where y_i are quadrature points and w_i are weighting factors. P_i and z_i are the values of property P and mole fractions for the pseudocomponents. Distribution parameters P_0 , A , and B are known from methods discussed in the previous section. Sets of y_i and w_i are tabulated for various numbers of quadrature points (e.g., see Abramowitz and Stegun, 1972, p 923). Table 2 lists values of y_i and w_i for 3 and 5 quadrature points.

The second method to obtain the pseudocomponents

Table 2. Gaussian Quadrature Points and Weights for 3 and 5 Points (from Abramowitz and Stegun, 1972; p 923)

i	point y	weight w_i
$N=3$		
1	0.415 774 556 783	$7.110\ 930\ 099\ 29 \times 10^{-1}$
2	2.294 280 360 279	$2.785\ 177\ 335\ 69 \times 10^{-1}$
3	6.289 945 082 937	$1.038\ 925\ 650\ 16 \times 10^{-2}$
$N=5$		
1	0.263 560 319 718	$5.217\ 556\ 105\ 83 \times 10^{-1}$
2	1.413 403 059 107	$3.986\ 668\ 110\ 83 \times 10^{-1}$
3	3.596 425 771 041	$7.594\ 244\ 968\ 17 \times 10^{-2}$
4	7.085 810 005 859	$3.611\ 758\ 679\ 92 \times 10^{-3}$
5	12.640 800 844 276	$2.336\ 997\ 238\ 58 \times 10^{-5}$

is by specifying the range of a property such as molecular weight or boiling point or the range of carbon number for each pseudocomponent. For example, a C_{7+} fraction can be divided into 5 pseudocomponents with carbon number ranges C_7-C_{10} , $C_{11}-C_{15}$, $C_{16}-C_{25}$, $C_{26}-C_{35}$, and C_{36+} . The lower and upper values of molecular weight for each group can be determined from the values given by Riazi and Al-Sahhaf, (1996). The molecular weight ranges are M_0-136 , $136-207$, $207-345$, $345-485$, and $485-\infty$. These ranges are arbitrary and may vary according to the number of pseudocomponents chosen. Having the lower and upper limits for each group, one can determine the mole fraction and molecular weight of the group using the probability density function:

$$z_i = \int_{P_{i-1}^*}^{P_i^*} F(P^*) dP^* \quad (23)$$

$$P_{i,\text{av}}^* = \left(\frac{1}{z_i} \right) \int_{P_{i-1}^*}^{P_i^*} P^* F(P^*) dP^* \quad (24)$$

where i varies from 1 to the total number of pseudocomponents. $P_{i,\text{av}}$ is the average value for property P for the pseudocomponent i . Substituting $F(P^*)$ from eq 4 into the above integrals, we get the following relations for the property $P_{i,\text{av}}$ and mole fraction z_i for the pseudocomponent i .

$$z_i = \exp\left(-\frac{B}{A} P_{i-1}^* B\right) - \exp\left(-\frac{B}{A} P_i^* B\right) \quad (25)$$

$$P_{i,\text{av}}^* = \left(\frac{1}{z_i} \right) \left(\frac{A}{B} \right)^{1/B} \left[\Gamma\left(1 + \frac{1}{B} q_{i-1}\right) - \Gamma\left(1 + \frac{1}{B} q_i\right) \right] \quad (26)$$

$$q_i = \frac{B}{A} P_i^* B \quad (27)$$

$$P_{i,\text{av}} = P_0 (1 + P_{i,\text{av}}^*) \quad (28)$$

where $\Gamma(1+1/B, q_i)$ is the incomplete gamma function which can be evaluated as discussed in various mathematical handbooks (e.g., Press et al., 1986; pp 160-161) or through computer software such as MATHEMATICA. If $B=1$, then eq 26 reduces to

$$P_{i,\text{av}}^* = \left(\frac{A}{z_i} \right) \left[\left(1 + \frac{P_{i-1}^*}{A} \right) \exp\left(-\frac{P_{i-1}^*}{A}\right) - \left(1 + \frac{P_i^*}{A} \right) \exp\left(-\frac{P_i^*}{A}\right) \right] \quad (29)$$

The two methods for splitting and lumping schemes described above may be summarized as follows:

Table 3. Evaluation of Proposed Methods for Prediction of Property Distributions of C₇₊ Samples in Table 1 (Number of Samples = 48; Number of Subfractions = 650)

	average absolute deviation (AAD)			
	<i>M</i>	<i>T</i> , K	<i>S</i>	<i>n</i>
method A	8.1	8	0.005	0.01
method B	4.3	4	0.005	0.01

Method I: Gaussian Quadrature Approach

1. Read composition of SCN groups and properties of plus fractions (e.g., M_{20+} and S_{20+}). Normalize the mole fractions.

2. If M and S for each SCN group are not available, obtain these properties from Riazi and Al-Sahhaf (1996).

3. Determine distribution parameters for molecular weight (M_0 , A_M , and B_M) in terms of cumulative mole fraction and for specific gravity (S_0 , A_S , and B_S) in terms of cumulative weight fraction.

4. Choose the number of pseudocomponents or lumped groups (e.g., 5) and determine their mole fractions (z_i) and molecular weights (M_i) from eqs 21 and 22 using the quadrature points given in Table 2.

5. Using molecular weights and mole fractions from step 4, determine discrete weight fractions (z_{wi}) for each pseudocomponent.

6. Convert discrete weight fractions into cumulative weight fractions and then use eq 1 with parameters S_0 and A_S from step 3 to obtain the specific gravity for each pseudocomponent. For example, S_1 (specific gravity of the first pseudocomponent) can be determined directly from eq 1 at $x_1 = z_{w1}/2$.

7. Obtain M_{av} and S_{av} for the mixture from $M_{av} = \sum z_i M_i$ and $1/S_{av} = \sum z_{wi}/S_i$.

Method II: Carbon Number Range Approach

1. Same as method I.

2. Same as method I.

3. Same as method I.

4. Choose the number of pseudocomponents (e.g., 5) and the carbon number ranges: C₇–C₁₀, C₁₁–C₁₅, C₁₆–C₂₅, C₂₆–C₃₅, C₃₆₊.

5. Obtain molecular weights for the carbon number ranges chosen in step 4 from Riazi and Al-Sahhaf (1996). The first molecular weight is M_0 . The molecular weight ranges are: M_0 –136, 136–207, 207–345, 345–485, and 485–∞.

6. Obtain mole fractions of pseudocomponents (z_i) from eq 25 and molecular weights (M_i) from eqs 26–28 or eq 29 if $B_M = 1$.

7. Same as step 5 in method I.

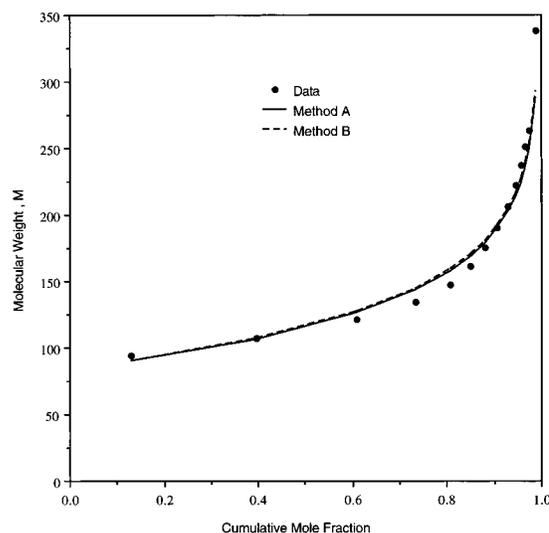
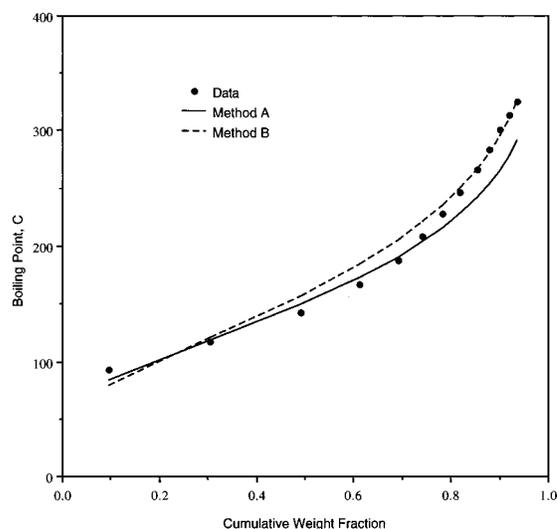
8. Same as step 6 in method I.

9. Same as step 7 in method I.

In this method if the calculated mole fraction for a pseudocomponent (in step 6) is too high or too low, we may reduce or increase the carbon number range chosen for that pseudocomponent in step 4. An example for use of these two methods is presented in the next section.

Results and Discussion

For samples listed in Table 1 parameters M_0 , A_M , T_0 , A_T , S_0 , A_S , I_0 , and A_I were predicted by both methods A and B. Errors produced for distribution of various properties for all 48 samples are given in Table 3. As is shown by the results in this table, for specific gravity and refractive index both methods A and B produced

**Figure 4.** Predicted distributions for molecular weight of sample no. 39.**Figure 5.** Predicted distributions for boiling point of sample no. 39.

nearly the same distributions with average deviations of about 0.6%. However, in using method B, since the TBP distribution was used, more accurate predictions for molecular weight and especially boiling point were obtained. Figures 4–7 show graphical evaluations with actual data for sample no. 39 whose properties are given in Table 1. The distribution of molecular weight versus cumulative mole fraction shown in Figure 4 is also presented in the form of a probability density function determined by eq 4 as shown in Figure 8. Results presented in Table 3 and Figures 4–8 indicate that both methods proposed here are capable of generating complete distributions for the four basic characterization parameters, namely, M , T_b , S , and I . Once these basic parameters are determined, then correlations of Riazi and Daubert (1980, 1987) can be used to estimate critical parameters needed in equations of state calculations.

To show an example for the lumping procedures as described in the previous section, we used analytical data available for sample no. 42 in Table 1. Molecular weight and specific gravities are available from C₇ to C₂₀₊ for 14 groups. Methods I and II described for the lumping and splitting procedures were used to obtain 5 pseudocomponents. Mole fractions, molecular weights,

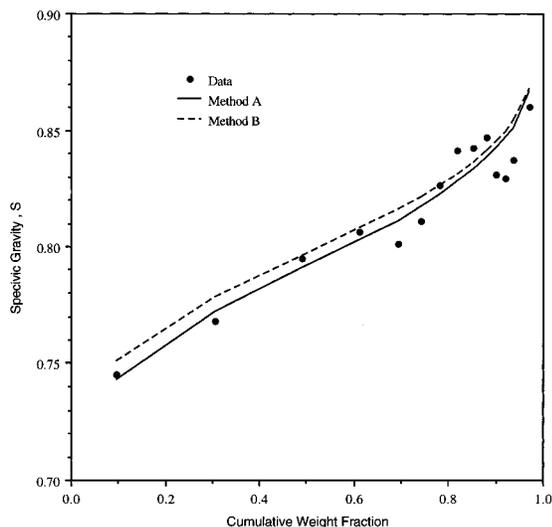


Figure 6. Predicted distributions for specific gravity of sample no. 39.

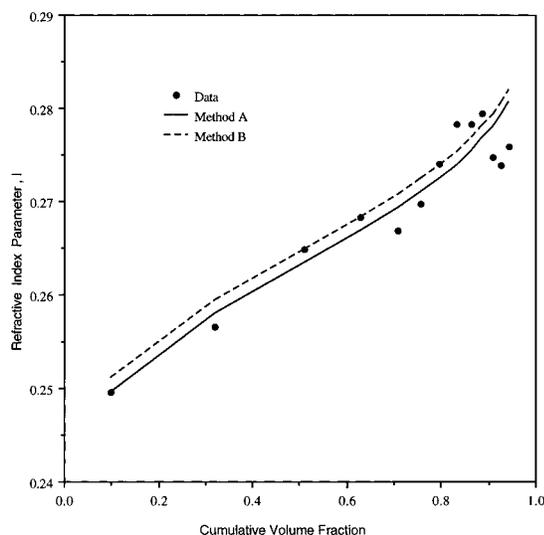


Figure 7. Predicted distributions for refractive index parameter of sample no. 39.

and specific gravities of these pseudocomponents are given in Table 4. Mixture average molecular weight and specific gravity calculated from the pseudocomponents are very close to the experimental values with deviations of about 0.1%.

For further evaluation of proposed methods, experimental data on boiling point distribution for a Russian crude oil as given by Ratzsch et al. (1988) were also used. In this case TBP distributions for feed, vapor, and liquid streams during flash distillation of the crude are available. Molecular weight, specific gravity, and refractive index of the mixture are 220, 0.8334, and 1.4626, respectively. If $F^F(T)$, $F^L(T)$, and $F^V(T)$ are the

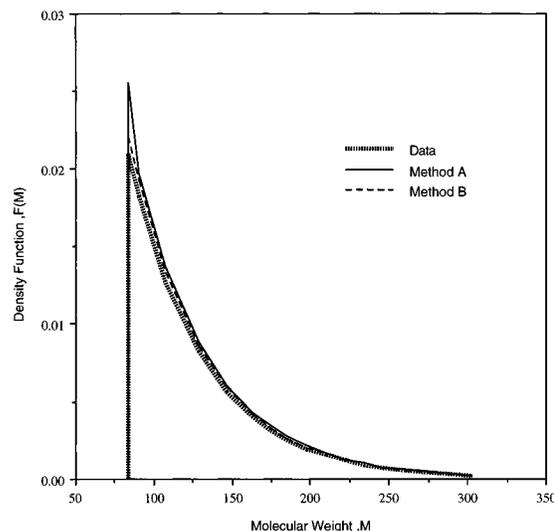


Figure 8. Predicted probability density function for molecular weight of sample no. 39.

probability density functions in terms of cumulative mole fraction for the boiling points of the feed, liquid, and vapor streams, respectively, then from material balance we have

$$F^F(T) = (1 - \phi)F^L(T) + \phi F^V(T) \quad (30)$$

in which ϕ is the mole ratio of vapor product to the feed. If the system is assumed to be ideal, then

$$[F^V(T) dT]p = [F^L(T) dT]p^*(T, T_S) \quad (31)$$

where p^* is the vapor pressure function for the fraction whose boiling point is T and its mole fraction in the vapor phase is $F^V(T) dT$. T_S is the temperature at which distillation occurs. The above relation can be written as

$$F^V(T) p = F^L(T) p^*(T, T_S) \quad (32)$$

For all three probability density functions, F^F , F^V , and F^L we have

$$\int_{T_0}^{\infty} F_T^F dT = \int_{T_0}^{\infty} F_T^V dT = \int_{T_0}^{\infty} F_T^L dT = 1 \quad (33)$$

From eqs 30, 32, and 33 one can derive the following relation for calculation of parameter ϕ :

$$\int_{T_0}^{\infty} \frac{p - p^*(T, T_S)}{(1 - \phi)p + \phi p^*(T, T_S)} F_T^F dT = 0 \quad (34)$$

Combination of Trouton's rule for the heat of vaporization and the Clausius–Clapeyron equation leads to the following relation for the vapor pressure:

Table 4. Lumping of 14 Fractions from C_7 to C_{20+} for Sample No. 42 into Five Pseudocomponents by Two Methods^a

pseudocomponent i	method I: Gaussian quadrature approach				method II: carbon number range approach			
	mol. frac. z_i	wt. frac. z_{wi}	M_i	S_i	mol. frac. z_i	wt. frac. z_{wi}	M_i	S_i
1	0.5218	0.3493	102.1	0.7436	0.532	0.372	106.7	0.7457
2	0.3987	0.4726	180.8	0.8023	0.302	0.328	165.5	0.7957
3	0.0759	0.1645	330.4	0.8591	0.144	0.240	254.4	0.8389
4	0.0036	0.0134	569.5	0.9174	0.019	0.049	392.7	0.8847
5	2.3×10^{-5}	1.42×10^{-4}	950.1	0.9809	0.003	0.011	553.5	0.9214
mixture			152.5	0.7905			152.5	0.7908

^a Experimental C_{7+} properties: $M_{7+} = 151.6$; $S_{7+} = 0.7917$. Distribution parameters: $M_0 = 84$; $A_M = 0.7157$; $B_M = 1$. For specific gravity in terms of the cumulative weight fraction: $S_0 = 0.655$, $A_S = 0.03875$, $B_S = 3$.

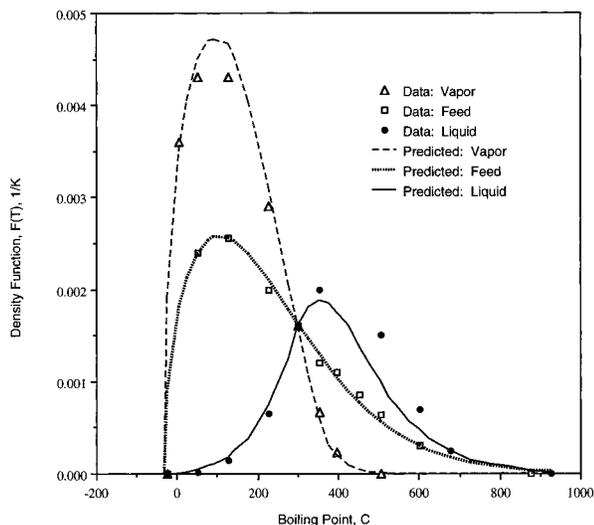


Figure 9. Predicted density functions of feed, liquid, and vapor at 300 °C for flash vaporization of a Russian crude oil. Actual data are taken from Ratzsch et al. (1988).

$$p^*(T, T_S) = p_a \exp[10.58(1 - T/T_S)] \quad (35)$$

where p_a is the atmospheric pressure. In this relation T is the boiling point of each cut in the distribution model. By combining eqs 30 and 32, we can get

$$F^L(T) = \frac{P}{(1 - \phi)p + \phi p^*(T, T_S)} F^F(T) \quad (36)$$

$$F^V(T) = \frac{p^*(T, T_S)}{(1 - \phi)p + \phi p^*(T, T_S)} F^F(T) \quad (37)$$

The proposed method has been applied to generate $F^F(T)$ and subsequently $F^L(T)$ and $F^V(T)$ from eqs 36 and 37, respectively. Parameters T_0 , A_T , and B_T for the feed which were obtained from method A are 241.7 K, 1.96, and 3, respectively. Results for the probability density functions are compared with the actual data (Ratzsch et al., 1988) in Figure 9. Results for flash distillation presented in Figure 9 are at 300 °C and 1 atm. Under these conditions parameter ϕ was calculated as 0.79 in which the actual value was 0.83. Part of errors for predicted distributions of $F^L(T)$ and $F^V(T)$ is due to assumption of an ideal solution for VLE calculations as well as an approximate relation for the estimation of vapor pressures. For more accurate calculations, the activity coefficient parameter can be included in the above relations by replacing $p^*(T, T_S)$ with $\gamma(T) p^*(T, T_S)$ where $\gamma(T)$ is the activity coefficient for species whose boiling point is T , and it may be estimated through methods such as the UNIFAC model.

Conclusions

In this work, based on a two-parameter distribution model, a method is presented to predict complete distributions for basic characterization parameters of a hydrocarbon-plus fraction. According to the proposed method, when three bulk properties (M , S , n) are available for a C_{7+} fraction, distribution functions for M , T_b , S , and I can be predicted with good accuracy. However, distributions can be predicted more accurately, if in addition to TBP data M and S are available. The method has been used to predict boiling point distributions of feed, vapor, and liquid products in flash distillation of a Russian crude oil sample, and predicted

TBP distributions were in good agreement with the experimental data. Finally splitting and lumping schemes of C_{7+} samples for the proposed distribution model are presented through application of the Gaussian quadrature technique or specification of the molecular weights of pseudocomponents. Estimated properties are in excellent agreement with the experimental data.

Nomenclature

- A, B = constants in eq 1
- C_1, C_2 = regression coefficients in eq 3
- d = density, g/cm³
- F = probability density function given by eq 4
- I = refractive index parameter defined in eq 2
- M = molecular weight
- n = refractive index at 20 °C and 1 atm
- P = property such as M , T_b , S , I , and d
- p = pressure
- p^* = vapor pressure
- q = parameter defined in eq 27
- S = specific gravity at 15.5 °C (60 °F)
- T = boiling point in distribution functions, K
- T_b = normal boiling point, K
- T_S = temperature at which distillation occurs, K
- X = regression parameter defined in eq 3
- x = cumulative volume, weight, or mole fraction
- Y = regression parameter defined in eq 3
- y_i = Gaussian quadrature points
- z_i = mole fraction of pseudocomponent i
- z_{wi} = weight fraction of pseudocomponent i
- w_i = Gaussian quadrature weighting factors

Greek Symbols

- ϵ = error parameter
- ϕ = vapor to feed mole ratio in single-stage flash distillation
- γ = activity coefficient of species in the mixture

Superscripts

- * = dimensionless parameter defined in eq 1 for property P as $P^* = (P - P_0)/P_0$
- F = feed in a distillation unit
- L = liquid product in a distillation unit
- V = vapor product in a distillation unit

Subscripts

- 0 = initial value for any property at $x = 0$
- a = atmospheric pressure
- av = average bulk property for the mixture
- I = refractive index parameter
- i = properties for a SCN group i
- i,av = average property for pseudocomponent i
- M = molecular weight parameter
- T = boiling point parameter
- S = specific gravity parameter

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