

APPLICATION OF THE GAMMA DISTRIBUTION MODEL TO MOLECULAR WEIGHT AND BOILING POINT DATA FOR PETROLEUM FRACTIONS

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(Received August 4, 1988; in final form August 3, 1988)

This paper applies the gamma distribution model for describing both the molar and boiling point distributions of heptanes-plus (C_{7+}) fractions. The three-parameter distribution model has been fit to TBP (true boiling point) data from forty-four samples of stabilized petroleum liquid (stock tank oil and condensate), obtained from separation of reservoir fluids. An excellent fit was achieved for both molar and boiling point distributions, though molar distribution seems to be more accurately described by the distribution model.

Two of the parameters, α and η , were correlated and fit to empirical equations for both molar and boiling point distributions. Since the third parameter, β , is defined in terms of α , η , and either average molecular weight or boiling point, it appears that a generalized correlation for molar and boiling point distributions may exist. We have not developed such correlations in this work, but our results provide the necessary groundwork for further research.

KEYWORDS Gamma distribution Molecular weight Boiling point Petroleum fractions.

Presented at the 1986 AIChE Annual Meeting, Miami, Florida, November 2–7.

INTRODUCTION

Petroleum reservoir fluids are complex mixtures made up of light compounds such as N_2 , CO_2 , H_2S , C_1 , and C_2 , intermediate hydrocarbons C_3 to C_6 , and heavier components with varying content of paraffinic, naphthenic, and aromatic compounds. Proper characterization of the heavier or "heptanes-plus" (C_{7+}) components is important when cubic equations of state (EOSs) are used to describe the complex phase behavior of reservoir fluids. The basis for most characterization methods is TBP data that includes mass, mole, and volume fractions of distillation cuts with measured molecular weight, specific gravity, and boiling point. Each distillation cut may be considered as a pseudocomponent with a critical pressure, critical temperature, and acentric factor. Correlations for estimating pseudocomponent critical properties are usually based on specific gravity and boiling point.

An alternative to characterizing the heptanes-plus fraction as a series of pseudocomponents is to use a probability model that expresses mole fraction as a continuous function of molecular weight. There are several advantages to using the continuous approach. First, the residue or heaviest C_{7+} cut can be readily divided into discrete fractions by extending the distribution to molecular weights greater than can be measured directly (Whitson, 1983a; Whitson and Torp, 1983). Another advantage is the definition of C_{7+} into a series of pseudocomponents based on statistical reasoning and the model parameters used to describe the molar distribution (Behrens and Sandler, 1986). A continuous description can also be used directly in the EOS (Briano and Glandt, 1984; Cotterman and Prausnitz, 1985; Cotterman *et al.*, 1985).

To describe C_{7+} as a continuous distribution requires that the model parameters be fit to experimental TBP data. This problem has received little attention in the literature and it is our purpose to introduce a procedure for fitting molar distribution by minimizing the sum of squares between experimental and model molecular weights (Whitson, 1983b). We also consider boiling point as a continuous distribution in terms of weight fraction and a similar procedure for fitting the distribution is proposed. More than forty samples have been described by the gamma distribution model using molecular weight and boiling point data from TBP analyses. All three parameters in the gamma distribution model are determined simultaneously to give a best fit of experimental data.

The fit of model parameters is to some extent dependent on the number and boiling-point range of distillation cuts. We checked the stability of best-fit parameters for each sample by varying the number of fractions from six to the actual number of distillation cuts. The behavior of best-fit model parameters was monitored and the stability was determined for each sample.

Finally, we found that two parameters of the model, α and η , are highly correlated for both molar and boiling point distributions. Empirical relations for α as a function of η are given for molar and boiling point distributions. This essentially reduces the number of model parameters to one. It also indicates that there may exist a general correlation for all three model parameters, α , η , and β in terms of C_{7+} properties.

DISTRIBUTION MODEL

The three-parameter gamma function (Type 3 of the Pearson system; Pearson, 1895) is used to describe the molar and boiling point distributions,

$$p(x) = \frac{(x - \eta)^{\alpha-1} \exp[-(x - \eta)/\beta]}{\beta^\alpha \Gamma(\alpha)} \tag{1}$$

where $p(x)$ is the probability density function. Parameter α defines the form of the distribution, η is the minimum value of x with a non-zero probability of occurrence, and β is a composite parameter defined in terms of α , η , and the average (or mean) value of x , x_{avg} ,

$$x_{avg} \equiv \alpha\beta + \eta \tag{2}$$

Molecular weight, M , is defined as the variable for molar distribution ($x \equiv M$) described by parameters α_M , η_M , and β_M . Boiling point, T_b , is defined as the variable for boiling point distribution ($x \equiv T_b$) described by parameters α_T , η_T , and β_T . Figure 1 shows the probability density function for molar distribution of two oil samples (Nos. 44 and 2 in Table I). Figure 2 shows the probability density function for boiling point distribution of an oil sample (No. 44) and a condensate sample (No. 28). Model parameters for the different samples are noted in the figures.

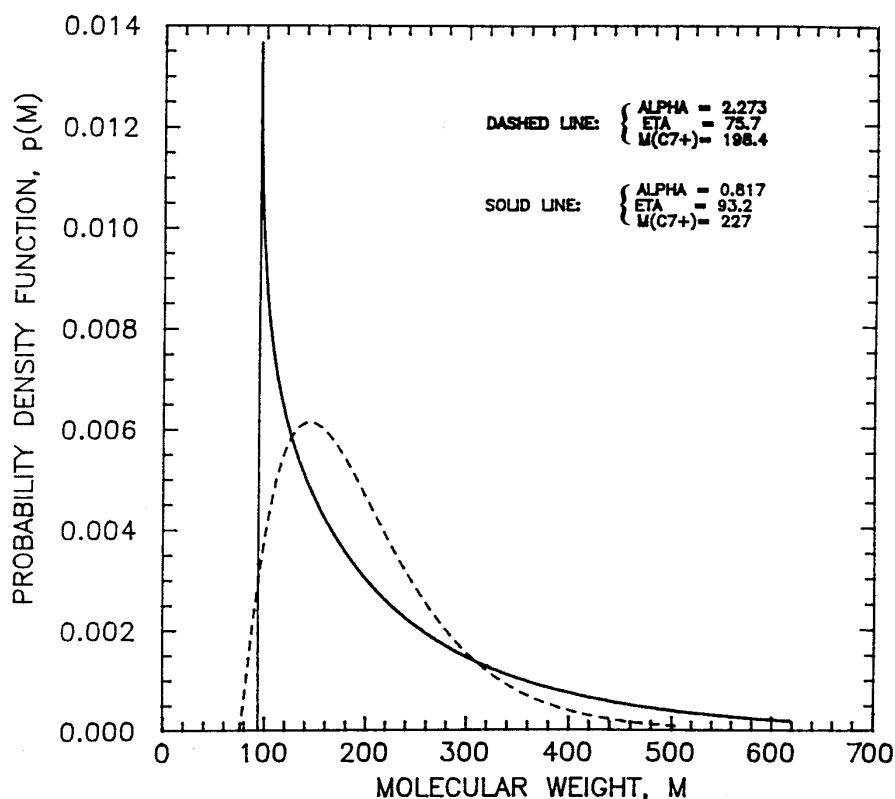


FIGURE 1 Probability density function vs. molecular weight for oil samples No. 2 (dashed line) and No. 44 (solid line).

Cumulative probability, $P(x)$, represents the area under the $p(x)$ curve from η to an upper boundary value, x ,

$$P(x) = \int_{\eta}^x p(x) dx \quad (3)$$

which can be shown to equal

$$P(x) = e^{-y} \sum_{j=0}^{\infty} [y^{\alpha+j} / \Gamma(\alpha + j + 1)] \quad (4)$$

with $y = (x - \eta) / \beta$. As x approaches ∞ the area sums to unity.

The average property, $x_{i, \text{avg}}$, in the interval x_{i-1} to x_i is expressed

$$x_{i, \text{avg}} = \frac{1}{P(x) - P(x_{i-1})} \left[\int_{\eta}^{x_i} xp(x) dx - \int_{\eta}^{x_{i-1}} xp(x) dx \right] \quad (5)$$

which can be shown to equal,

$$x_{i, \text{avg}} = \eta + \alpha\beta \frac{P_1(x_i) - P_1(x_{i-1})}{P(x_i) - P(x_{i-1})} \quad (6)$$

The function $P_1(x)$ is evaluated by starting the summation in Eq. (4) at $j = 1$ instead of $j = 0$.

MOLAR DISTRIBUTION

For molar distribution, we define $P(x)$ as cumulative normalized mole fraction,

$$P(M_i) \equiv \frac{\sum_{j=1}^i z_j}{\sum_{j=1}^N z_j} \quad (7)$$

where M_i is the upper bound of molecular weight for distillation cut i , and z_j is the mole fraction of cut j , where $j = 1, \dots, N$ and N is the total number of C_{7+} fractions. For the last fraction, $M_N = \infty$. Normalized mole fraction, z_i , for an individual cut is given by,

$$z_i = P(M_i) - P(M_{i-1}) \quad (8)$$

Average molecular weight, M_i , of cut i is given by Eq. (6),

$$M_i = \eta_M + \alpha_M \beta_M \frac{P_1(M_i) - P_1(M_{i-1})}{P(M_i) - P(M_{i-1})} \quad (9)$$

Normalized weight fraction can be expressed as

$$w_i = z_i M_i / (\eta_M + \alpha_M \beta_M) \quad (10)$$

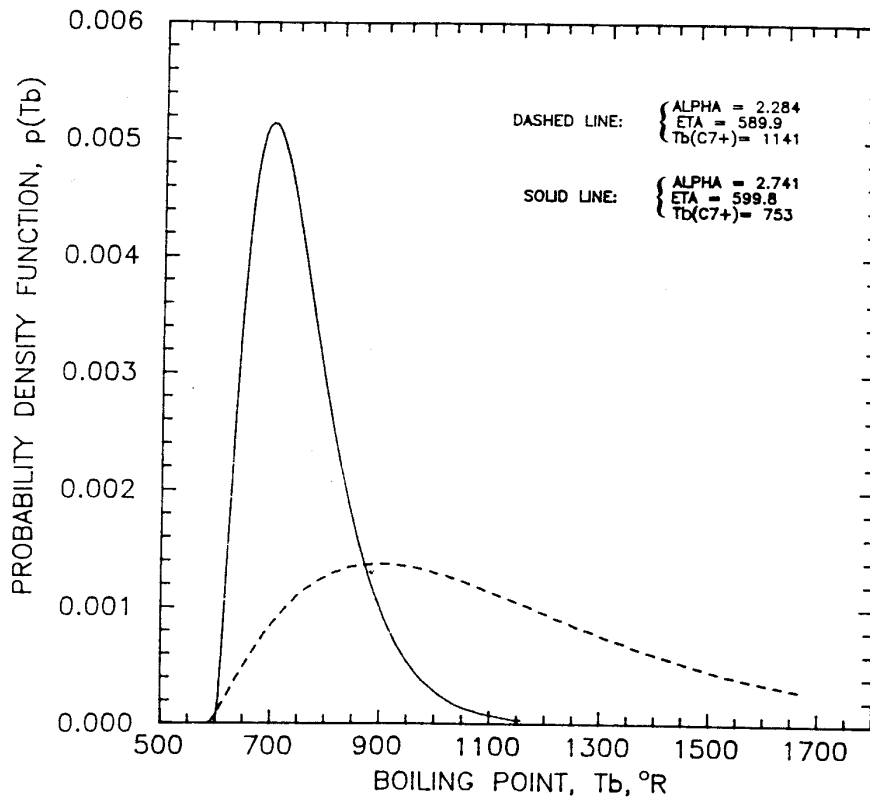


FIGURE 2 Probability density function vs. boiling point for condensate sample No. 28 (solid line) and oil sample No. 44 (dashed line).

Experimental TBP data is fit to the molar distribution model using measured weight fractions and molecular weights. The procedure is outlined below:

1. Calculate experimental normalized weight fraction for each distillation cut

$$w_{i, \text{exp}} = \frac{(z_i M_i)_{\text{exp}}}{\sum_{j=1}^N (z_j M_j)_{\text{exp}}} \quad (11)$$

This calculation is only performed once since results can be stored.

2. Assume distribution parameters α_M , η_M , and β_M . For the first guess, assume $\eta_M = 88$, $\alpha_M = 1.0$, and β_M estimated from Eq. (2) [$\beta_M = (M_{7+} - \eta_M) / \alpha_M$] using experimental M_{7+} .

3. Assume an upper molecular weight boundary, M_i , for the fraction. Calculate $P(M_i)$ and z_i from the distribution model, Eqs. (4) and (8). Calculate average molecular weight, M_i , and normalized weight fraction, w_i , from Eqs. (9) and (10).

4. If model weight fraction does not equal experimental weight fraction within an acceptable tolerance (e.g., 10^{-7}), adjust the upper molecular weight bound, M_i , and return to step 3. A Newton or chord method can be used to solve the trial and error problem.

5. Repeat the trial and error procedure in steps 3 and 4 for all fractions except

the last one. Calculate the sum of squares function,

$$E_M(\alpha_M, \beta_M, \eta_M) = \sum_{i=1}^{N-1} \left[\frac{M_{i,\text{exp}} - M_{i,\text{model}}}{M_{i,\text{exp}}} \right]^2 \quad (12)$$

where $M_{i,\text{exp}}$ and $M_{i,\text{model}}$ are experimental and model molecular weights, respectively.

6. Minimize E_M by adjustment of model parameters α_M , η_M , and β_M using a non-linear regression model.

7. Calculate model average molecular weight using Eq. (2) and compare with the experimental value. We generally find the model value is within a few percent of the measured value.

8. Compare model molecular weight and mole fraction of each fraction with experimental values to establish the accuracy of the model fit.

BOILING POINT DISTRIBUTION

For the boiling point distribution model we define cumulative probability as cumulative normalized *weight* fraction,

$$P(T_{bi}) \equiv \frac{\sum_{j=1}^i w_{j,\text{exp}}}{\sum_{j=1}^N w_{j,\text{exp}}} \quad (13)$$

The normalized weight fraction of a cut determined from the distribution model is then,

$$w_i = P(T_{bi}) - P(T_{bi-1}) \quad (14)$$

Weight-average T_{bi} is calculated from Eq. (6),

$$T_{bi} = \eta_T + \alpha_T \beta_T \frac{P_1(T_{bi}) - P_1(T_{bi-1})}{P(T_{bi}) - P(T_{bi-1})} \quad (15)$$

The procedure for matching model parameters α_T , η_T , and β_T to experimental TBP data is outlined below:

1. Calculate experimental normalized weight fraction, $w_{i,\text{exp}}$, for each fraction from Eq. (11). This calculation is only performed once since results can be stored.

2. Assume distribution parameters α_T , η_T , and β_T . For the first guess, assume $\eta_T = 640(^{\circ}\text{R})$, $\alpha_T = 1.0$, and β_T estimated from Eq. (2) [$\beta_T = (T_{b7+} - \eta_T)/\alpha_T$]. An estimate of T_{b7+} (in $^{\circ}\text{R}$) can be made using experimental M_{7+} and the approximate relation

$$T_{b7+} = 20.853 M_{7+}^{0.75093} \quad (16)$$

This equation was developed using model values of T_{b7+} and M_{7+} from the three-parameter fits of the forty-four samples.

3. Assume an upper boiling point boundary, T_{bi} , for the fraction. Calculate $P(T_{bi})$ and w_i from the distribution model, Eqs. (4) and (14). Calculate average boiling point, T_{bi} , from Eq. (15).

4. If model weight fraction does not equal experimental weight fraction within an acceptable tolerance (e.g., 10^{-7}), adjust the upper boiling point bound, T_{bi} , and return to step 3.

5. Repeat the trial and error procedure in steps 3 and 4 for all fractions except the last one. Calculate the sum of squares function,

$$E_T(\alpha_T, \beta_T, \eta_T) = \sum_{i=1}^{N-1} \left[\frac{T_{bi, \text{exp}} - T_{bi, \text{model}}}{T_{bi, \text{exp}}} \right]^2 \quad (17)$$

where $T_{bi, \text{exp}}$ and $T_{bi, \text{model}}$ are experimental and model boiling points, respectively.

6. Minimize E_T by adjustment of model parameters α_T , η_T , and β_T using a non-linear regression model.

7. Compare the model boiling point of each fraction with the experimental value to establish the accuracy of the model fit.

APPLICATION OF THE DISTRIBUTION MODELS

The distribution models for molecular weight and boiling point have been applied to 44 petroleum samples having complete TBP analyses. The samples represent oil types ranging from light condensate to heavy oil. The number of distillation cuts ranges from six to 26, and most samples are distilled according to an ASTM standard with boiling point intervals of normal paraffins (Katz and Firoozabadi, 1978).

Table I summarizes the average properties of each sample. Model parameters determined by the three-parameter regressions are also listed. In general the distributions give an excellent fit of the experimental data. Figures 3 and 4 plot model distributions of an oil and gas condensate (sample Nos. 44 and 28), respectively. The absolute average residual, AAR, is used to quantify the goodness of the model fit,

$$\text{AAR}_M = \frac{1}{(N-1)} \sum_{i=1}^{N-1} |M_{i, \text{calc}} - M_{i, \text{exp}}| \quad (18)$$

$$\text{AAR}_T = \frac{1}{(N-1)} \sum_{i=1}^{N-1} |T_{bi, \text{calc}} - T_{bi, \text{exp}}| \quad (19)$$

where the last C_{7+} fraction is not included in AAR values given in Table I.

For oil sample No. 44, $\text{AAR}_M = 1$ kg/mol and the difference between experimental and model average molecular weight is about 2.5%: $M_{7+, \text{exp}} = 233$ and $M_{7+, \text{model}} = 227$. Boiling point distribution is also represented reasonably well, as indicated by an $\text{AAR}_T = 5^\circ\text{R}$. The gas condensate sample No. 28 also has an $\text{AAR}_M = 1$ kg/mol for the molecular weight distribution, with experimental and model average molecular weights essentially equal. The boiling point model fit has an $\text{AAR}_T = 2^\circ\text{R}$.

The boiling point distribution fit for Hoffman *et al.*'s (1953) oil sample did not converge. It appears that η_T tends to zero and α_T tends to infinity, indicating a normal distribution. This is seen in Figure 5, where $p(T_b)$ is plotted for $\alpha_T = 23.5$

TABLE I
Heptanes-plus properties and distribution parameters for condensate and oil samples for three-parameter fit

Sample No.	Sample I.D.	No. C ₇₊ Fractions	Fluid type	Measured heptanes-plus data		Est. Watson char. factor Kw	Boiling point		Three-parameter fit		Molecular weight					
				Mol. weight	Specific gravity		Alpha	Eta	Alpha	Eta	Alpha	Eta				
1	Standing-Katz	7	BO	228.5	0.8682	11.71	6.984	202.0	1143	12	U	0.740	82.72	224.0	4	U
2	Hoffman <i>et al.</i>	24	BO	198.7	0.8409	11.78	Best-Fit not found (Alpha > 20)			9	U	2.273	75.69	198.4	2	S
3	Jacoby <i>et al.</i> (a)	7	GC	142.8	0.7717	12.05	10.079	389.5	871	1	U	2.385	79.16	143.3	1	U
4	Jacoby <i>et al.</i> (b)	7	GC	180.7	0.7902	12.24	1.281	585.3	1027	1	U	0.508	91.74	186.6	5	U
5	Lee <i>et al.</i> 1	6	BO	289.4	0.9041	11.73	2.843	454.9	1385	2	S	1.168	77.68	246.7	7	U
6	Lee <i>et al.</i> 2	6	BO	206.2	0.8505	11.74	2.946	478.6	1129	0	S	0.764	88.27	198.6	1	U
7	Lee <i>et al.</i> 3	6	BO	348.2	0.9386	11.69	4.402	494.9	1410	1	U	2.062	77.51	290.1	2	U
8	Hariu and Sage	15	BO	217.5	0.8448	11.90	2.991	488.5	1111	10	U	0.553	97.28	218.9	3	S
9	RRI: Austad <i>et al.</i>	15	GC	177.5	0.8067	12.00	1.595	629.9	952	3	S	0.763	97.38	171.7	2	S
10	Haaland Sample A	16	BO	257.2	0.8732	11.87	1.911	581.8	1266	4	S	1.149	81.88	245.6	1	S
11	Haaland Sample B	15	BO	205.8	0.8412	11.84	1.319	627.0	1133	5	U	0.778	84.00	202.0	1	S
12	Haaland Sample C	15	BO	257.8	0.8955	11.62	1.466	636.1	1360	4	S	0.926	82.98	261.5	1	S
13	Berge 1	16	BO	256.1	0.8759	11.83	1.989	598.7	1223	6	S	0.819	99.45	244.7	6	U
14	Pedersen BO-1	14	BO	210.9	0.8459	11.83	1.356	616.6	1168	6	U	0.600	96.91	208.8	2	S
15	Pedersen BO-2	14	BO	226.0	0.8536	11.86	1.336	612.1	1293	9	U	0.596	91.26	229.6	2	S
16	Pedersen BO-3	17	BO	254.0	0.8842	11.72	2.290	567.8	1241	7	U	0.836	92.01	243.7	2	U
17	Pedersen BO-4	17	BO	217.1	0.8457	11.88	2.115	567.8	1127	10	U	0.794	88.78	212.0	1	S
18	Pedersen BO-5	17	BO	236.2	0.8533	11.95	1.990	584.5	1161	9	U	0.872	94.91	227.9	5	S

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19	Pedersen BO-6	17	BO	264.7	0.8695	11.96	2.229	579.8	1175	7	S	1.292	85.51	254.2	8	U
20	Pedersen BO-7	14	BO	232.0	0.8666	11.76	1.800	592.8	1216	9	U	0.763	93.31	228.5	2	S
21	Pedersen BO-8	14	BO	230.3	0.8658	11.76	1.738	594.8	1217	10	U	0.741	93.44	227.2	2	S
22	Pedersen BO-9	13	BO	230.5	0.8564	11.87	1.454	612.3	1232	6	U	0.654	96.20	223.7	2	U
23	Pedersen BO-10	14	BO	210.5	0.8448	11.84	1.352	615.8	1167	7	U	0.596	96.83	208.4	2	S
24	Pedersen BO-11	24	BO	213.6	0.8458	11.85	2.137	575.6	1118	7	S	0.809	87.21	210.8	4	S
25	Pedersen BO-12	15	BO	227.7	0.8542	11.87	2.015	586.5	1181	9	U	0.807	91.56	225.4	3	U
26	Pedersen GC-1	11	GC	149.4	0.8184	11.54	0.843	645.9	918	1	S	0.464	96.75	148.9	2	U
27	Pedersen GC-2	5	GC	120.2	0.7962	11.43	1.485	628.7	792	0	U	1.017	86.38	120.5	0	U
28	Pedersen GC-3	12	GC	118.9	0.7604	11.87	2.741	599.8	753	2	S	0.949	92.38	118.8	1	S
29	Pedersen GC-4	12	GC	149.9	0.8172	11.57	0.896	638.9	917	6	U	0.431	96.63	148.3	2	S
30	Pedersen GC-5	12	GC	150.5	0.8169	11.58	0.812	640.6	930	5	U	0.397	96.78	149.0	2	S
31	Pedersen GC-6	26	GC	149.7	0.8201	11.53	2.945	530.0	892	18	U	0.627	92.25	149.5	3	S
32	Pedersen GC-7	14	GC	157.1	0.8094	11.74	0.895	635.7	970	8	U	0.445	93.63	156.2	2	S
33	Midget No.1	12	GC	129.1	0.7865	11.68	1.144	639.8	793	3	U	0.735	93.71	129.6	1	S
34	Midget No.2	14	BO	214.0	0.8598	11.69	2.889	558.9	1137	11	U	1.201	80.41	213.6	3	S
35	Albuskjell No.1	19	GC	170.6	0.8005	12.00	1.999	589.1	983	8	U	0.659	93.21	169.6	4	U
36	Albuskjell No.2	19	GC	169.2	0.8008	11.98	1.809	592.8	992	12	U	0.589	92.54	168.5	3	S
37	Albuskjell No.3	19	GC	153.7	0.7871	11.98	2.436	570.1	914	11	U	0.690	91.71	153.1	3	S
38	Albuskjell No.4	19	GC	176.5	0.8043	12.02	1.675	601.8	1019	7	S	0.587	94.88	175.4	3	S
39	Albuskjell No.5	19	GC	175.2	0.8033	12.02	1.905	590.2	999	8	U	0.599	96.72	174.4	3	S
40	Eldfisk No.1	13	BO	219.7	0.8517	11.83	1.642	611.5	1165	4	U	0.941	86.06	213.3	1	S
41	Eldfisk No.2	14	BO	219.9	0.8554	11.79	1.882	592.2	1164	10	U	0.866	87.63	217.7	2	U
42	Eldfisk No.3	11	BO	232.1	0.8601	11.84	1.377	627.7	1290	2	S	0.724	93.11	228.0	1	S
43	Eldfisk No.4	5	BO	256.0	0.8626	11.98	1.219	631.9	1486	0	U	1.161	89.63	222.6	0	U
44	Ekofisk No.1	24	BO	232.9	0.8534	11.92	2.284	589.9	1141	5	S	0.817	93.16	227.0	1	S

Notes:

1. Estimated Watson characterization factor from equation by Whitson²¹ based on Riazi-Daubert molecular weight correlation.
2. Samples 9-44 are from North Sea oil and gas condensate reservoirs. Other samples are taken from the literature. North Sea samples 9-32 are detailed in published references or reports.
3. Fluid type BO refers to "black oil" and GC refers to "gas condensate" reservoir fluids.

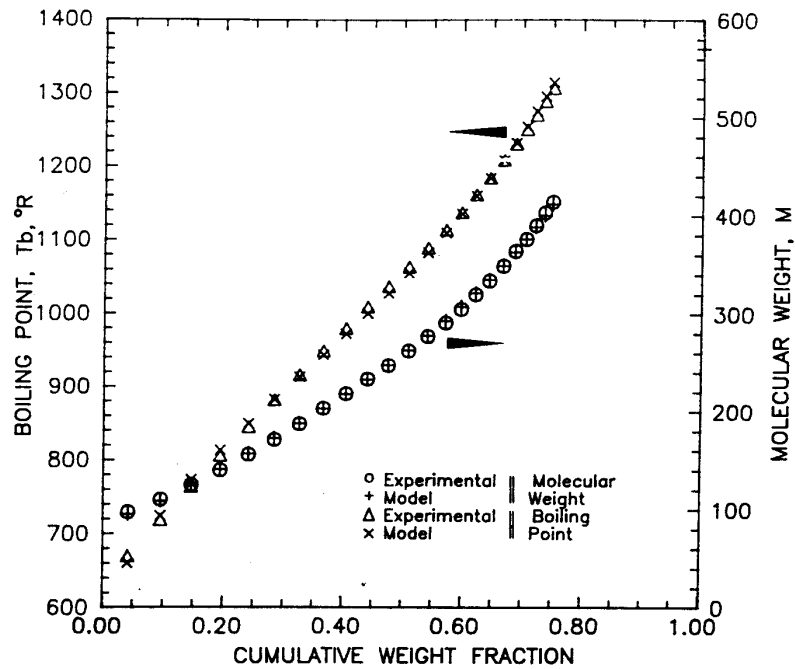


FIGURE 3 Fit of model distribution parameters to experimental boiling point and molecular weight data for oil sample No. 44.

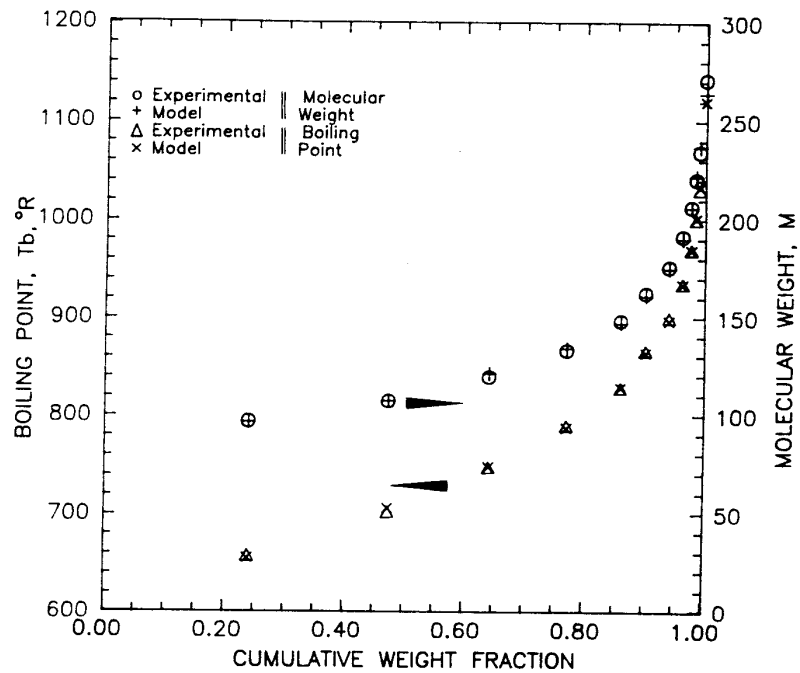


FIGURE 4 Fit of model distributions to experimental boiling point and molecular weight data for condensate sample No. 28.

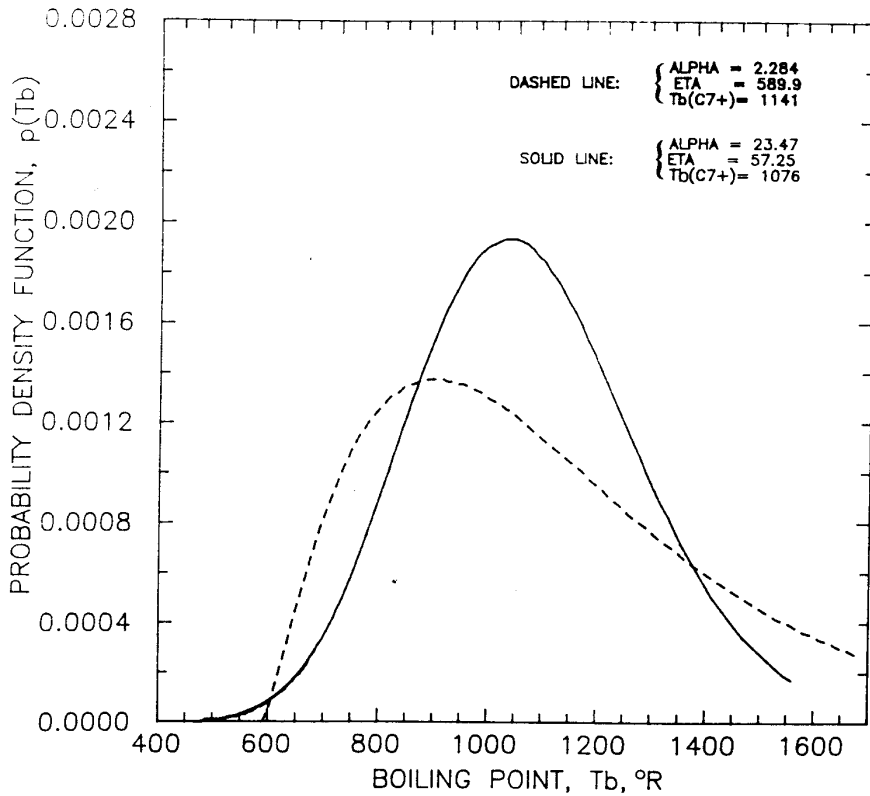


FIGURE 5 Probability density function vs. boiling point for oil samples No. 2 (solid line) and No. 44 (dashed line). The fit to boiling point data for sample No. 2 did not converge.

and $\eta_T = 57^\circ\text{R}$ which is the largest α value obtained before numerical problems in the calculation algorithm occurred; a plot of $p(T_b)$ for the best fit of oil sample No. 44 is shown for comparison.

Analysis of model parameters for the 44 samples indicates that α and η are strongly correlated, as shown in Figures 6 and 7 for boiling point and molar distributions, respectively. Empirical relations describing the approximate relation of α and η are proposed,

$$\eta_T = 658.0 \left[1 - \frac{1}{1 + \frac{27.467}{\alpha_T^{1.659}}} \right] \quad (20)$$

and

$$\eta_M = 110.0 \left[1 - \frac{1}{1 + \frac{4.043}{\alpha_M^{0.723}}} \right] \quad (21)$$

These equations were then used and a two-parameter fit of the experimental data was performed. Parameters α and β were fit, where η was correlated to α by Eqs. (20) and (21). Table II summarizes results of the two-parameter model fits. It is seen that some loss in accuracy results from using the empirical relations, but the model fits are still very good.

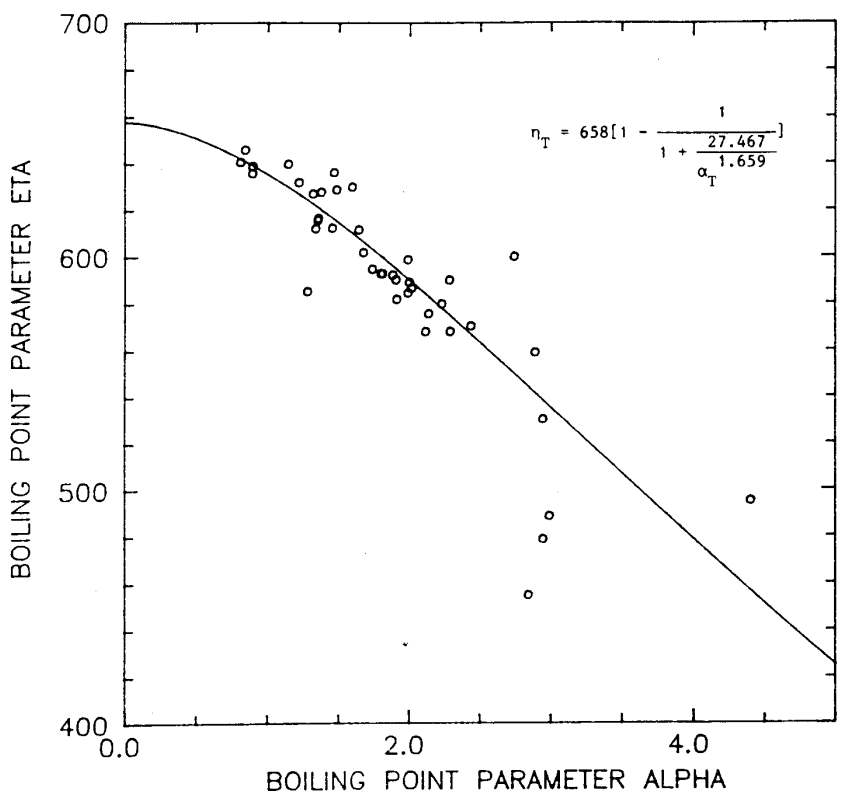


FIGURE 6 Boiling point distribution parameter correlation and best-fit results for 43 petroleum samples (No. 2 not included).

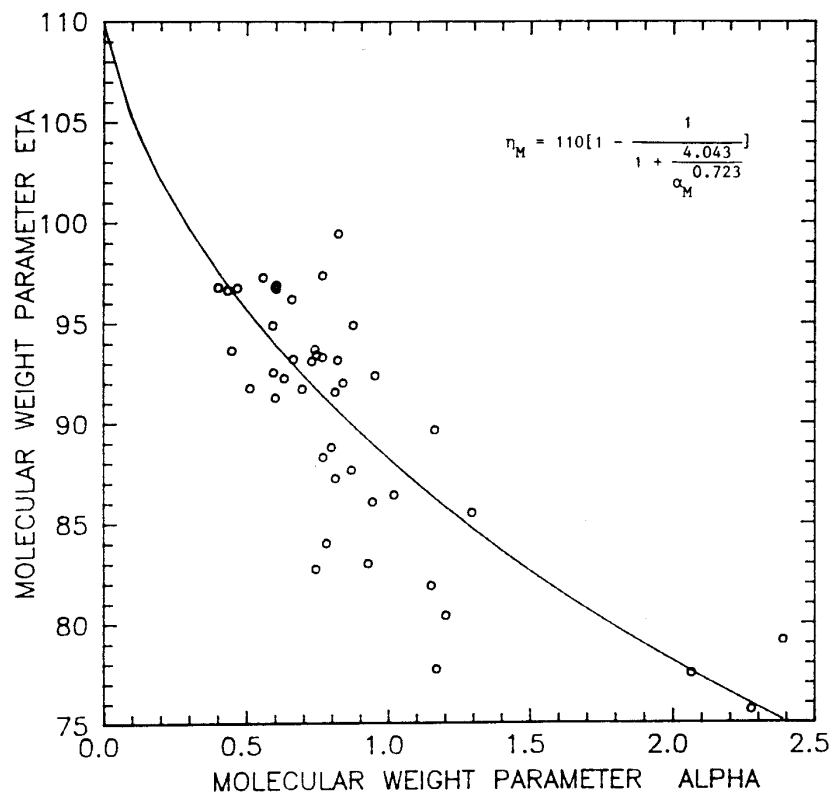


FIGURE 7 Molecular weight distribution parameter correlation and best-fit results for 44 petroleum samples.

TABLE II

Heptanes-plus properties and distribution parameters for condensate and oil samples for two-parameter fit

Sample No.	Sample I.D.	No. C ₇₊ Fractions	Fluid type	Measured heptanes-plus data		Est. Watson char. factor Kw	Boiling point		Two-parameter fit		Molecular weight
				Mol. weight	Specific gravity		Alpha	T _{b7+}	With alpha-eta correlations		
									Alpha	AAR	
1	Standing-Katz	7	BO	228.5	0.8682	11.71	1.703	1200	0.636	227.6	5
2	Hoffman <i>et al.</i>	24	BO	198.7	0.8409	11.78	—	—	2.259	198.4	2
3	Jacoby <i>et al.</i> (a)	7	GC	142.8	0.7717	12.05	2.483	903	3.314	142.5	9
4	Jacoby <i>et al.</i> (b)	7	GC	180.7	0.7902	12.24	0.753	1115	0.473	189.0	5
5	Lee <i>et al.</i> 1	6	BO	289.4	0.9041	11.73	1.277	1584	0.908	252.9	7
6	Lee <i>et al.</i> 2	6	BO	206.2	0.8505	11.74	1.442	1182	0.703	200.1	2
7	Lee <i>et al.</i> 3	6	BO	348.2	0.9386	11.69	10.721	1323	2.056	290.2	2
8	Hariu and Sage	15	BO	217.5	0.8448	11.90	1.997	1117	0.574	217.7	4
9	RRI: Austan, <i>et al.</i>	15	GC	177.5	0.8067	12.00	1.846	949	0.887	169.4	3
10	Haaland Sample A	16	BO	257.2	0.8732	11.87	1.689	1282	1.048	247.4	2
11	Haaland Sample B	15	BO	205.8	0.8412	11.84	1.380	1129	0.680	205.4	2
12	Haaland Sample C	15	BO	257.8	0.8955	11.62	1.718	1335	0.841	264.6	2
13	Berge 1	16	BO	256.1	0.8759	11.83	2.145	1217	0.994	240.8	6
14	Pedersen BO-1	14	BO	210.9	0.8459	11.83	1.307	1172	0.637	207.1	2
15	Pedersen BO-2	14	BO	226.0	0.8536	11.86	1.237	1307	0.569	231.5	2
16	Pedersen BO-3	17	BO	254.0	0.8842	11.72	2.131	1247	0.864	243.0	2
17	Pedersen BO-4	17	BO	217.1	0.8457	11.88	1.802	1136	0.761	212.9	1
18	Pedersen BO-5	17	BO	236.2	0.8533	11.95	1.878	1165	0.966	226.1	5
19	Pedersen BO-6	17	BO	264.7	0.8695	11.96	2.259	1175	1.310	254.1	8
20	Pedersen BO-7	14	BO	232.0	0.8666	11.76	1.679	1223	0.794	227.5	2
21	Pedersen BO-8	14	BO	230.3	0.8658	11.76	1.607	1226	0.768	226.3	2

(continued)

TABLE II—(continued)

Sample No.	Sample I.D.	No. C ₇₊ Fractions	Fluid type	Measured heptanes-plus data			Est. Watson char. factor Kw	Two-parameter fit				
				Mol. weight	Specific gravity	Boiling point		With alpha-eta correlations		Molecular weight		
						Alpha		T _{b7+}	Alpha	MW7+	Alpha	MW7+
22	Pedersen BO-9	13	BO	230.5	0.8564	11.87	1.400	1237	0.701	221.8	6	2
23	Pedersen BO-10	14	BO	210.5	0.8448	11.84	1.291	1172	0.631	206.7	7	2
24	Pedersen BO-11	24	BO	213.6	0.8458	11.85	2.006	1120	0.767	212.1	8	4
25	Pedersen BO-12	15	BO	227.7	0.8542	11.87	1.958	1184	0.820	225.0	9	3
26	Pedersen GC-1	11	GC	149.4	0.8184	11.54	0.901	915	0.470	148.6	2	2
27	Pedersen GC-2	5	GC	120.2	0.7962	11.43	1.170	804	1.251	119.9	5	1
28	Pedersen GC-3	12	GC	118.9	0.7604	11.87	1.731	736	1.134	116.8	16	2
29	Pedersen GC-4	12	GC	149.9	0.8172	11.57	0.899	917	0.428	148.5	6	2
30	Pedersen GC-5	12	GC	150.5	0.8169	11.58	0.804	930	0.389	149.6	5	2
31	Pedersen GC-6	26	GC	149.7	0.8201	11.53	2.708	895	0.613	150.2	18	3
32	Pedersen GC-7	14	GC	157.1	0.8094	11.74	0.871	972	0.420	158.2	8	2
33	Midget No.1	12	GC	129.1	0.7865	11.68	1.294	789	0.780	128.6	4	2
34	Midget No.2	14	BO	214.0	0.8598	11.69	3.041	1143	1.060	215.4	11	4
35	Albuskjell No.1	19	GC	170.6	0.8005	12.00	1.976	983	0.662	169.5	8	4
36	Albuskjell No.2	19	GC	169.2	0.8008	11.98	1.693	993	0.572	169.3	12	3
37	Albuskjell No.3	19	GC	153.7	0.7871	11.98	2.486	913	0.677	153.5	11	3
38	Albuskjell No.4	19	GC	176.5	0.8043	12.02	1.608	1021	0.596	175.1	7	3
39	Albuskjell No.5	19	GC	175.2	0.8033	12.02	1.816	1000	0.636	173.1	8	3
40	Eldfisk No.1	13	BO	219.7	0.8517	11.83	1.714	1161	0.876	214.7	4	2
41	Eldfisk No.2	14	BO	219.9	0.8554	11.79	1.811	1167	0.824	218.8	10	3
42	Eldfisk No.3	11	BO	232.1	0.8601	11.84	1.505	1272	0.746	227.2	2	1
43	Eldfisk No.4	5	BO	256.0	0.8626	11.98	1.300	1462	1.742	206.8	2	1
44	Ekofisk No.1	24	BO	232.9	0.8534	11.92	2.579	1138	0.848	226.2	5	1

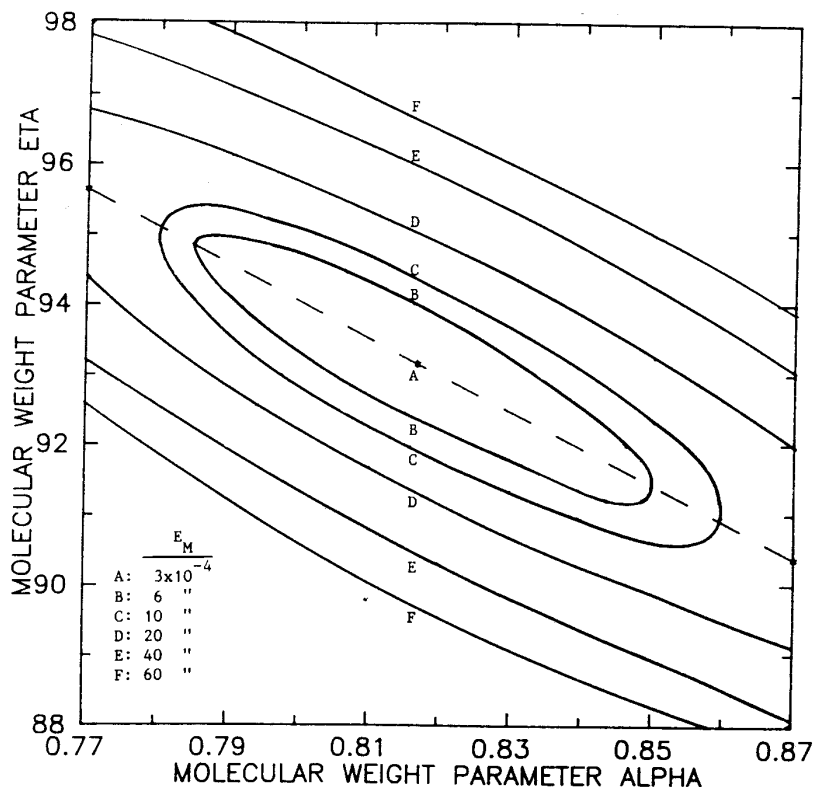


FIGURE 8 Contour plot of the error function for molecular weight distribution for oil sample No. 44. Dashed line indicates the general direction of correlation for parameters alpha and eta.

The strong correlation between α and η is also seen from the shape of the error functions, E_M and E_T . Figure 8 shows several contours of E_M plotted on an (α, η) grid for sample No. 44. The model average molecular weight was held constant to eliminate one degree of freedom from the minimization problem, however this did not affect the general shape of the contours. We see a long valley along which several combinations of α and η give a reasonable match of the data. This general behavior should be considered when choosing a non-linear regression algorithm to determine model parameters.

A good model fit depends to some extent on the number of C_{7+} fractions reported for a sample. We studied this effect for each sample by fitting the three model parameters using fewer and fewer fractions, where the heaviest fraction was modified to maintain correct C_{7+} properties. Figure 9 shows parameters α_M , η_M , and model N_{7+} as a function of the number of distillation cuts included in the match. Unstable behavior is observed for matches with less than 16 fractions for this sample. However, the variation of model parameters is not large, and the values determined using only six fractions do not deviate substantially from the stable parameter values. Table I indicates when parameter estimates using all experimental data for a given sample are stable (S) or unstable (U). Figure 10 shows a plot of α_M versus η_M for the varying number of C_{7+} fractions. The general correlation (Eq. 21) is also drawn on the figure as a solid line. The dashed

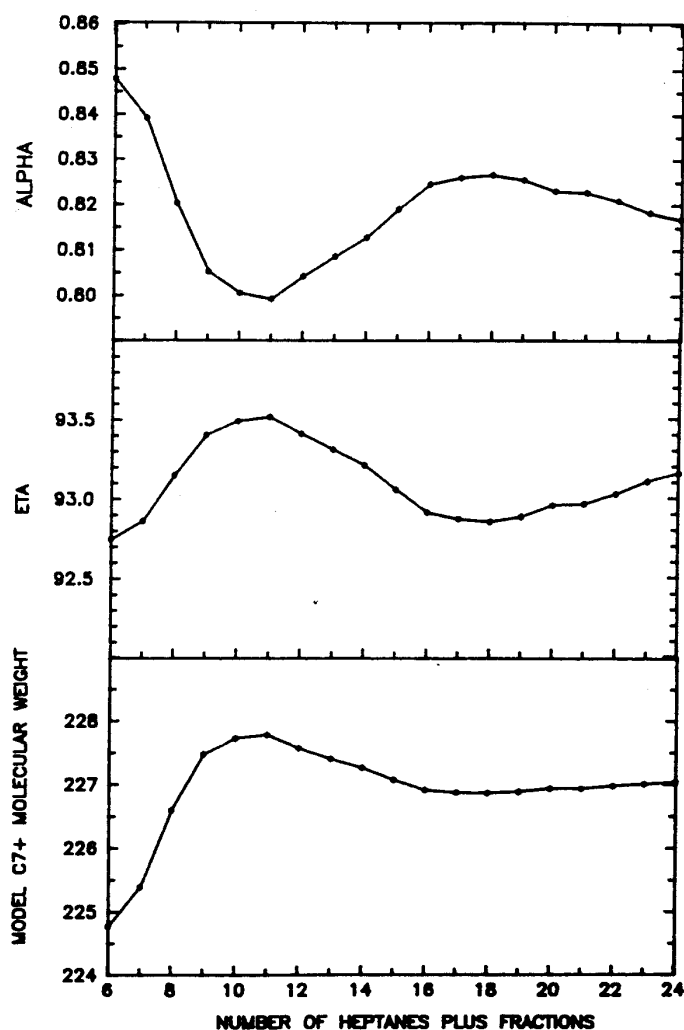


FIGURE 9 Molar distribution parameters resulting from three-parameter fit using various numbers of distillation cuts for oil sample No. 44.

line represents the minimum along the valley shown in the error function plot in Figure 8.

DISCUSSION

Results from this study indicate that the three-parameter gamma distribution model can, with reasonable accuracy, be used to describe molar and boiling point distributions of heptanes-plus fractions. The choice of molar distribution in terms of molecular weight and mole fraction, and boiling point distribution in terms of boiling point and weight fraction gives a direct link between the two distributions. That is, when distribution models for molecular weight and boiling point have been determined, the C_{7+} fraction can be split into discrete pseudocomponents

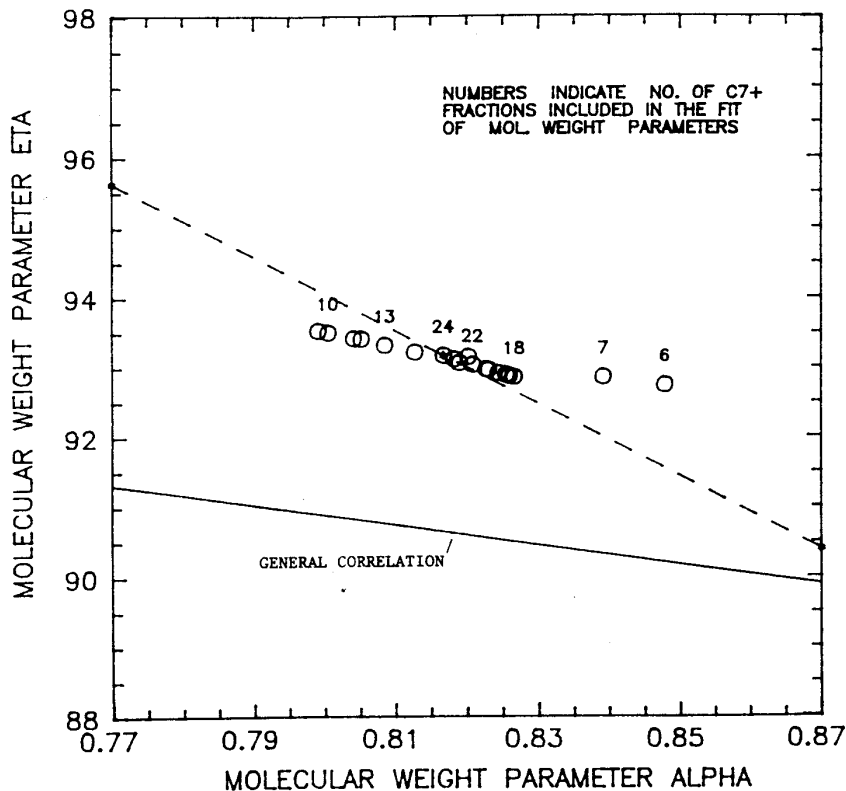


FIGURE 10 Cross correlation plot of molecular weight distribution parameters using various numbers of distillation cuts for sample No. 44. Dashed line refers to the valley shown in Fig. 8, while the solid line represents the general correlation (Eq. (20)).

for which the weight and mole fractions, molecular weight, and boiling point are readily calculated.

A natural extension of this work would be to accurately estimate specific gravity of a fraction from molecular weight and boiling point distributions. This was tried using both the Riazi-Daubert (1980) and Twu (1984) correlations, but results were inconclusive and they are therefore not presented. We should mention, however, that even using experimental molecular weights and boiling points did not result in accurate specific gravity estimates with the Riazi-Daubert and Twu correlations. Consistent correlation of molecular weight, boiling point, and specific gravity using the proposed distribution models is a natural extension of our present research.

CONCLUSIONS

We have shown that experimental TBP data can be characterized by molar and boiling point distributions using the three-parameter gamma function. Forty-four C₇₊ samples ranging from light condensate to heavy oil are characterized by the proposed distribution model. General correlations relating two of the distribution

parameters (α and η) are suggested for molar and boiling point distributions. Ongoing research is aimed at linking specific gravity to the molecular weight and boiling point distributions.

ACKNOWLEDGEMENTS

This work was supported by research grants from NAVF (Norwegian Research Council for Science and the Humanities) and Saga Petroleum a.s.

NONEMCLATURE

AAR	absolute average residual
E	error function
M	molecular weight, kg/mol
\bar{M}	upper bound on molecular weight, kg/mol
M_i	average molecular weight of fraction i , kg/mol
M_{7+}	average molecular weight of heptanes-plus, kg/mol
N	number of distillation cuts
$P(x)$	cumulative probability function
$P_1(x)$	cumulative probability function
$p(x)$	probability density function
T_b	normal boiling point, °R
\bar{T}_b	upper bound on normal boiling point, °R
T_{bi}	average normal boiling point of fraction i , °R
w_i	normalized weight fraction
x_{avg}	calculated average property of heptanes-plus
x	probability function variable (M or T_b)
\bar{x}	upper bound on variable x
y	probability function variable
z_i	normalized mole fraction of fraction i

Subscripts

model	model property
exp	experimental property
i	distillation cut index
M	molar distribution
7 +	heptanes-plus

T boiling point distribution

Greek Letters

α, β, η parameters in gamma distribution function
 Γ gamma function
 γ specific gravity (water = 1)

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