

Distribution Model for Properties of Hydrocarbon-Plus Fractions

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A versatile equation is used to describe the cumulative weight, mole, or volume fraction (x) with various properties (P) of petroleum fractions (eq 1), with $P^* = (P - P_0)/P_0$, where P denotes the boiling point (T_b), specific gravity (S), refractive index parameter (I), or molecular weight (M). For a given property, the value of B is approximately constant for most crude oil and gas condensate samples: $T_b(B_T \approx 1.5)$, $S(B_S \approx 3)$, $I(B_I \approx 3)$, and $M(B_M \approx 1)$. Therefore, only two unknowns must be determined for a given property distribution: A and P_0 . The fitting procedure is straightforward and can be performed with linear regression of the form $Y = C_1 + C_2X$ where $Y = \ln P^*$ and $X = \ln \ln [1/(1-x)]$. The proposed procedure has been tested on more than 80 crude oil and condensate samples from around the world. Finally, once the fit has been made, the eq 1 can be applied as a continuous distribution in terms of a probability density function.

In characterization and thermophysical property prediction of crude oils and hydrocarbon plus fractions (e.g., C_{7+} fractions containing C_7 and heavier hydrocarbons), knowledge of accurate values for various characterization parameters such as boiling point, specific gravity, refractive index, and molecular weight is quite important. Once these parameters are known, then correlations such as those given by Kesler and Lee (1976) or Riazi and Daubert (1980a, 1987) can be used for prediction of critical properties and other thermodynamic properties for the mixture. However, the major difference between the characterization of crude oils and narrow boiling range petroleum fractions is that, for crude oils, mixture bulk properties cannot be directly used to estimate the thermophysical properties of the mixture. While for narrow boiling fractions, mixture properties such as the average boiling point, specific gravity, molecular weight, or refractive index may directly be used to predict many other properties as outlined in Chapters 2 and 4 of the *API Technical Data Book—Petroleum Refining* (1983).

One of the most successful methods of characterizing crude oils is use of the γ distribution model for molecular weight of plus fractions as proposed by Whitson (1983a,b). This molar distribution model is represented by the three-parameter γ function as follows:

$$F(M) = \frac{(M - \eta)^{\alpha-1} \exp\left[-\frac{M - \eta}{\beta}\right]}{\beta^\alpha \Gamma(\alpha)}$$

where $F(M)$ is the probability density function, M is the molecular weight, and α , β , and η are distribution parameters. Whitson et al. (1986) have shown application of the above model to both the molecular weight and the boiling point of crude oils and gas condensates. The three parameters in the above correlation are different for each property and each sample.

In this work, we propose a new approach in characterization of crude oils, gas condensates, and petroleum fractions with a simple and general model for all properties.

Technical Development

A data bank on various properties of 68 C_{7+} fractions has been collected at the Norwegian Institute of Technology of the University of Trondheim (Whitson et al., 1986). For 68 fractions listed in Table I, information on the boiling point, molecular weight, and specific gravity for each hydrocarbon group is available in addition to the volume and weight percent of each group. The number of hydrocarbon groups as well as the residue (heaviest

hydrocarbon group in the fraction) weight percent for various samples are also given in Table I. Experimental data on the specific gravity, molecular weight, and boiling point then were tabulated in terms of cumulative weight or mole fraction for each sample. From extensive analysis of data on these samples, the following generalized equation was found to be the most suitable fit for all properties:

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

where

$$P^* = \frac{P - P_0}{P_0} \quad x^* = 1 - x$$

P is the absolute boiling point (T_b), molecular weight (M), or specific gravity (S). x is the cumulative weight, mole, or volume fraction. P_0 is the parameter specific for each property (T_0 , S_0 , M_0) and each sample. A is the parameter specific for each property (A_T , A_S , A_M) and each sample. B is the parameter specific for each property (B_T , B_S , B_M) but the same for all samples.

For most samples $B_S = 3$, $B_M = 1$, and $B_T = 1.5$. For the boiling point and specific gravity, x = cumulative weight fraction is used in eq 1, and for molecular weight, x = cumulative mole fraction is used in eq 1. With the above fixed values for B for each property, eq 1 reduces to a two-parameter equation with parameters P_0 and A to be determined from experimental data.

Equation 1 can be converted into the following linearized form:

$$Y = C_1 + C_2X \quad (2)$$

where

$$Y = \ln P^* \quad X = \ln \ln (1/x^*)$$

By comparing eq 2 with eq 1, we have

$$B = 1/C_2$$

$$A = B \exp(C_1B) \quad (3)$$

For samples with the residue weight percent greater than 30%, the residue data were not included in the regression. When a fixed value of B is used for each property, only C_1 in eq 2 is used to estimate parameter A from eq 3.

To estimate P_0 in eq 1, a trial-and-error procedure can be used. By choosing a value for P_0 , which must be lower than the value of P for the first data point in the data set, parameter A can be determined from linear regression of the data. Parameter P_0 is determined by minimizing the sum of squared errors.

The values of P_0 and A for specific gravity, boiling point, and molecular weight for all 68 samples in Table I were

Table I. Crude Oil and Gas Condensates Used in This Work

sample	sample id	no. of C ₇₊ fractions	fluid residue		M ₇₊	S ₇₊
			type ^a	weight, %		
1	Standing-Katz (1942)	7	BO	29	228.5	0.8682
2	Hoffmann et al. (1953)	24	GC	6	198.7	0.8409
3	Jacoby et al. (1959), a	7	BO	22	142.8	0.7717
4	Jacoby et al. (1959), b	6	BO	58	193.3	0.7995
5	Lee et al. (1979), 1	6	BO	60	289.4	0.9041
6	Lee et al. (1979), 2	6	BO	39	206.2	0.8505
7	Lee et al. (1979), 3	6	BO	68	348.2	0.9386
8	RRI: Austad et al. (1983)	15	BO	21	177.5	0.8067
9	Hariu and Sage (1969)	14	BO	13	227.5	0.8518
10	Haaland (1981), A	16	BO	51	257.2	0.8732
11	Haaland (1981), B	15	BO	38	205.7	0.8412
12	Haaland (1981), C	15	BO	56	257.8	0.8955
13	Berge (1981), 1	16	BO	47	256.1	0.8759
14	Pedersen BO-1 ^b	14	BO	44	210.9	0.8451
15	Pedersen BO-2 ^b	14	BO	51	226.0	0.8528
16	Pedersen BO-3 ^b	17	BO	47	254.0	0.8834
17	Pedersen BO-4 ^b	17	BO	35	217.1	0.8449
18	Pedersen BO-5 ^b	17	BO	39	236.2	0.8525
19	Pedersen BO-6 ^b	17	BO	41	264.7	0.8687
20	Pedersen BO-7 ^b	14	BO	49	232.0	0.8658
21	Pedersen BO-8 ^b	14	BO	47	230.3	0.8650
22	Pedersen BO-9 ^b	13	BO	51	230.5	0.8564
23	Pedersen BO-10 ^b	14	BO	44	210.5	0.8448
24	Pedersen BO-11 ^b	24	BO	25	213.6	0.8458
25	Pedersen BO-12 ^b	15	BO	45	227.7	0.8542
26	Pedersen GC-1 ^b	11	GC	26	149.4	0.8195
27	Pedersen GC-2 ^b	5	GC	33	120.2	0.7955
28	Pedersen GC-3 ^b	12	GC	1	118.9	0.7597
29	Pedersen GC-4 ^b	12	GC	22	149.9	0.8165
30	Pedersen GC-5 ^b	12	GC	24	150.5	0.8162
31	Pedersen GC-6 ^b	26	GC	3	149.7	0.8201
32	Pedersen GC-7 ^b	14	GC	23	155.4	0.8086
33	Midget 1	12	GC	6	129.1	0.7865
34	Midget 2	14	BO	44	214.0	0.8598
35	Albuskjell 1	19	GC	17	170.6	0.8005
36	Albuskjell 2	19	GC	18	169.2	0.8008
37	Albuskjell 3	19	GC	9	153.7	0.7871
38	Albuskjell 4	19	GC	22	176.5	0.8043
39	Albuskjell 5	19	GC	19	175.2	0.8033
40	North Sea 1	13	BO	48	216.7	0.8517
41	North Sea 2	14	BO	44	219.9	0.8554
42	North Sea 3	11	BO	60	232.1	0.8601
43	North Sea 4	5	BO	85	256.0	0.8626
44	North Sea 5	24	BO	25	232.9	0.8534
45	North Sea BO-1	24	BO	34	242.9	0.8833
46	North Sea BO-2	24	BO	25	211.4	0.8458
47	North Sea BO-3	14	BO	57	243.4	0.8602
48	North Sea BO-4	14	BO	45	211.2	0.8459
49	North Sea BO-5	13	BO	51	229.0	0.8569
50	North Sea BO-6	5	BO	71	173.2	0.8372
51	North Sea BO-7	14	BO	62	266.5	0.8606
52	North Sea BO-8	14	BO	62	269.1	0.8797
53	North Sea BO-9	24	BO	34	247.9	0.8830
54	North Sea BO-10	14	BO	47	221.5	0.8338
55	North Sea GC-1	5	GC	36	125.3	0.7737
56	North Sea GC-2	14	GC	7	132.1	0.8039
57	North Sea GC-3	14	GC	5	128.4	0.7909
58	North Sea GC-4	14	GC	12	132.6	0.8048
59	North Sea GC-5	14	GC	30	172.0	0.8127
60	North Sea GC-6	14	GC	19	151.6	0.7917
61	North Sea GC-7	11	GC	2	122.5	0.7633
62	North Sea GC-8	14	GC	15	140.1	0.8068
63	North Sea GC-9	14	GC	22	170.5	0.8113
64	North Sea GC-10	14	GC	26	175.2	0.8055
65	North Sea GC-11	12	GC	2	119.3	0.7838
66	North Sea 6	9	BO	79	278.6	0.9039
67	North Sea 7	14	BO	62	267.8	0.9033
68	North Sea 8	9	GC	36	163.8	0.8137

^a BO, black oil; GC, gas condensate. ^b Pedersen et al., 1984a-c.

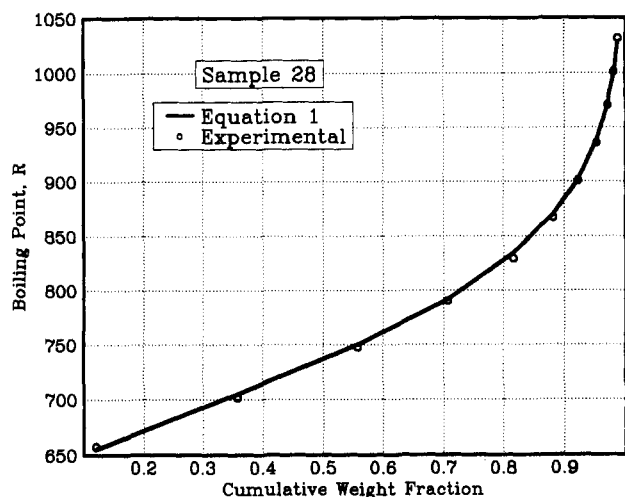
determined with eq 1 and a constant B for each property.

By use of this technique with the best values for parameter B of 3, 1.5, and 1 for S , T_b , and M , respectively, the overall average absolute deviation for specific gravity

is 0.005 (0.6%), for boiling point is 7 °F (0.7%), and for molecular weight is 4 (2.2%). When values of B were determined separately for each sample to give a best fit of the data, absolute average deviations for the boiling

Table II. Evaluation of the Proposed Method and the γ Distribution Model for Estimation of Properties of Samples Listed in Table I

property	absolute av dev ^a		
	proposed method (eq 1)		γ distrib model
	2-param	3-param	
M	4.09 (2.2%)	2.28 (1.2%)	2.31 (1.2%)
T_b , °F	7.26 (0.7%)	5.78 (0.56%)	6.53 (0.63%)
S	0.005 (0.6%)	0.005 (0.6%)	0.01 (1.24%) ^b

^a AAD = $(1/N) \sum |\text{estimated property} - \text{experimental property}|$.^b Estimated from constant Watson K procedure (Whitson, 1983a, b).**Figure 1.** Evaluation of eq 1 for the boiling point of sample 28 in Table I ($T_0 = 616$, $A = 0.1859$, $B = 1.5$).

point and molecular weight reduced to 5.8 °F (0.56%) and 2.3 (1.2%), respectively. For specific gravity, the best value for B remained the same as in the case of the two parameter fit ($B_S = 3$). In table II, a summary is given of the results when using eq 1 for both cases of two- and three-parameter fits, as well as comparison with the γ distribution mode. From these evaluations, it is clear that the new distribution model with three parameters (eq 1) is similar to the three-parameter γ distribution model for both boiling point and molecular weight.

As Whitson (1984) has described, the specific gravity distribution can be determined from a constant Watson K procedure. As it is shown in Table II, this procedure results in an average absolute deviation of 0.01 (1.2%) compared to 0.005 (0.6%) when using eq 1. Errors involved with the specific gravity estimation almost proportionally increase the errors in estimation of other properties, such as critical properties, which in turn would greatly increase the errors in estimation of the final thermophysical properties as described by Brule et al. (1985).

Figure 1 shows the estimated boiling point from eq 1 versus the experimental values for sample 28 in Table I.

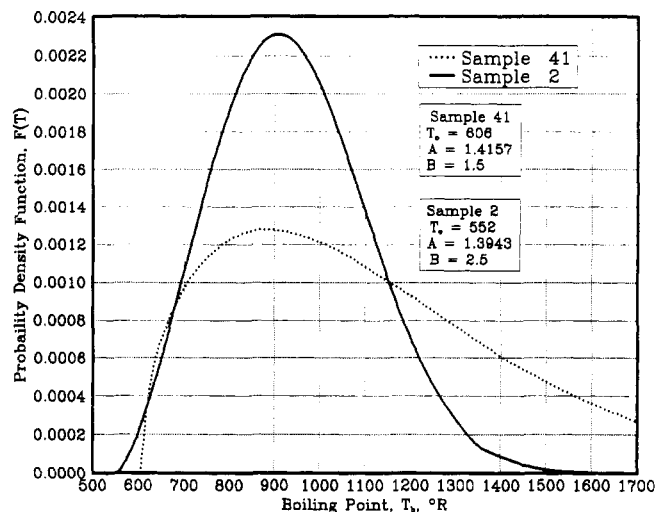
Probability Density Function for Various Properties. If the probability function in terms of P^* is shown with $F(P^*)$, then we must have

$$\int_0^\infty F(P^*) dP^* = 1 \quad (4)$$

After rearranging eq 1 and differentiating with respect to P^* , $F(P^*)$ can be obtained as follows:

$$F(P^*) = \frac{B^2}{A} P^{*B-1} \exp\left(-\frac{B}{A} P^{*B}\right) \quad (5)$$

Figure 2 shows the probability density function for the

**Figure 2.** Probability density function for the boiling point of sample 41 and sample 2.**Table III. Evaluation of the Proposed Model for Estimation of Mixture Average Properties for the 68 Samples Listed in Table I**

property	AAD		
	proposed model (eq 7 and 14)		
	2-param	3-param	γ distrib model
M	12.58 (6.8%)	11.9 (6.4%)	5.4 (2.9%)
S	0.003 (0.35%)	0.003 (0.35%)	

boiling point of two samples.

Once $F(P^*)$ is known for a property of a mixture, the average value for the property can be obtained from the following relation:

$$P^*_{av} = \int_0^\infty P^* F(P^*) dP^* \quad (6)$$

Substituting eq 5 for $F(P^*)$ and evaluating the above integration for the average property give

$$P^*_{av} = (A/B)^{1/B} \Gamma(1 + 1/B) \quad (7)$$

If fixed values of B are used for the molecular weight, boiling point, and specific gravity with $B_M = 1$, $B_T = 1.5$, and $B_S = 3$, we obtain the following expressions for the average values of these properties:

$$M^*_{av} = A_M \quad (8)$$

$$T^*_{av} = 0.689 A_T^{2/3} \quad (9)$$

$$S^*_{av} = 0.619 A_S^{1/3} \quad (10)$$

In the above relations, the distributions for molecular weight, boiling point, and specific gravity are in terms of the cumulative mole, weight, and volume fractions, respectively.

If the specific gravity is given in terms of cumulative weight fractions, then the average specific gravity of the mixture is calculated as follows:

$$\frac{1}{S_{av}} = \int_0^1 \frac{dx_w}{S}$$

or in terms of $F(S^*)$

$$\frac{1}{S^*_{av} + 1} = \int_0^\infty F(S^*) \frac{dS^*}{S^* + 1} \quad (11)$$

If the integration on the right-hand side of the above equation is given by J , then after numerical evaluation of

Table IV. Estimation of the Refractive Index and Density of Petroleum Mixtures by Using the Proposed Model

property	type of samples	hydrocarbon group (eq 1)		mixture property (eq 7 and 14)		type of x used in the model	ref
		no. of data points	AAD	no. of samples	AAD		
I at 20 °C	oil fractions	162	0.0026 (0.18%)	13	0.002 (0.14%)	volume fraction	Berge (1981); Smith (1968)
I at 20 °C	oil fractions	57	0.0028 (0.19%)	4	0.0022 (0.15%)	weight fraction	Berge (1981)
d at 20 °C, g/cm ³	C ₆₊ fractions	57	0.004 (0.52%)	4	0.0 (0.0%)	volume fraction	Berge (1981)
d at 20 °C, g/cm ³	C ₆₊ fractions	57	0.005 (0.64%)	4	0.0023 (0.27%)	weight fraction	Berge (1981)

this integral, we obtain the following expressions for J in terms of A_S :

for $0.05 \leq A_S \leq 0.4$

$$1/J = 1.3818 + 0.3503A_S - 0.1932A_S^2 + 0.059 \ln A_S \quad (12)$$

for $0.005 \leq A_S \leq 0.05$

$$1/J = 1.25355 + 1.44886A_S - 5.97771A_S^2 + 0.02951 \ln A_S$$

For the samples listed in Table I, values of A_S normally were between 0.05 and 0.4.

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

$$P_{av} = P_0(1 + P^*_{av}) \quad (13)$$

Table III shows a summary of results for the estimation of the average molecular weight and the specific gravity of samples listed in Table I. The estimated average specific gravities from eq 12 were very close to the experimental values given in Table I.

Figure 3 shows a molecular weight distribution measured recently by Rodgers et al. (1987). Estimated values using both the proposed equation (eq 1) and the γ distribution model are also shown in Figure 3. However, for this residue sample, the best value for B_M was 2.5 and the weight-average molecular weight calculated through eq 7 and 14 (with $A_M = 71.64$ and $M_0 = 144$) for this sample is 632.8, which is in excellent agreement with the measured weight-average molecular weight of 630.

Two other important parameters in the estimation of thermophysical properties of hydrocarbons are refractive index and density. As described by Riazi and Daubert (1980b, 1986), both refractive index and density are two necessary parameters in the prediction of molecular-type analysis (paraffin, naphthene, and aromatic content of a fraction) as well as other properties. The same distribution model for the specific gravity proposed in this work can also be applied to the refractive index and density. As described by Riazi and Daubert (1980a, 1987), the refractive index can be correlated through parameter I defined as

$$I = \frac{n^2 - 1}{n^2 + 2} \quad (14)$$

where n is the sodium D-line refractive index at 20 °C and 1 atm of pressure. A summary of the results for the estimation of both refractive index and density is given in Table IV when the distributions are represented in terms of the cumulative weight and volume fractions. For both refractive index and density, parameter B was the same as for the specific gravity; that is, $B_I = B_d = B_S = 3$ for all samples. Therefore, for the refractive index, density, and specific gravity eq 1 reduces to the two-parameter correlation with $B = 3$.

Conclusions

In this work, a simple, generalized, two-parameter equation in the form of eq 1 is proposed for estimation of

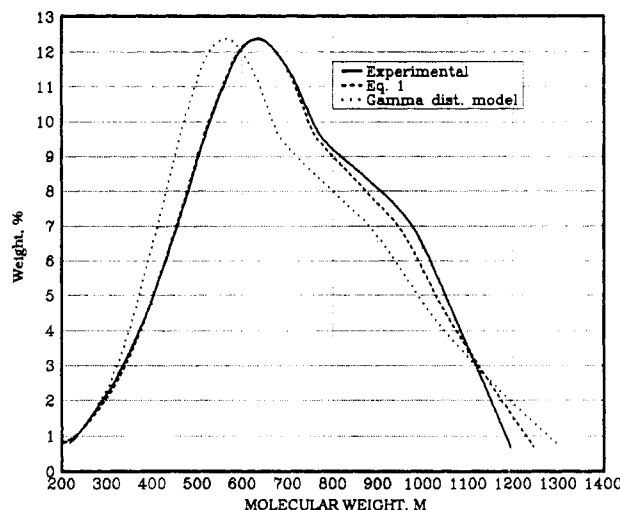


Figure 3. Molecular weight distribution of the heavy residue (Rodgers et al., 1987).

the basic characterization parameters of crude oils and plus fractions. Cumulative weight, volume, and mole fraction can be used in this model. The model predicts very good average specific gravities, refractive indexes, and densities for the mixture in terms of both cumulative weight and volume fractions.

The accuracy of eq 1 for boiling points and molecular weights can be improved if it is used in terms of a three-parameter equation with variable B . However, it has been found that for each group of crudes a common B value for the molecular weight or boiling point can be obtained.

Inspection of the results obtained in this work indicates that there is an excellent relationship between the initial values of the various properties, P_0 's, for molecular weight, boiling point, refractive index, and specific gravity when parameter B is fixed for each property. Such relations are important in the estimation of all property distributions from known average properties such as molecular weight, specific gravity, and refractive index.

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Nomenclature

A, B = constant parameters defined in eq 1
 C_1, C_2 = regression coefficients in eq 2
 d = density, g/cm³
 F = probability density function defined in eq 10
 E = error defined in eq 4
 I = refractive index parameter defined in eq 5
 J = integration parameter defined in eq 12
 M = molecular weight
 N = number of data points used in the regression of eq 2
 n = refractive index at 20 °C and 1 atm

P = property such as T_b , M , I , and d
 S = specific gravity
 T_b = normal boiling point, °R
 X = regression parameter defined in eq 2
 x = cumulative volume, weight, or mole fraction
 Y = regression parameter defined in eq 2

Superscript

* = dimensionless parameter defined for property P as $P^* = (P - P_0)/P_0$

Subscripts

av = average property for the mixture
 0 = initial value for any parameter at $x = 0$
 i = hydrocarbon group in the mixture
 I = refractive index parameter
 M = molecular weight parameter
 T = boiling point parameter
 S = specific gravity parameter

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COMMUNICATIONS

The Flow Field of Annular Jets at Moderate Reynolds Numbers

The flow field of single annular jets was studied at Reynolds numbers ranging from 3400 to 21 500. The three annular nozzles used in the study had a square-edged entrance configuration and length-to-diameter ratios of 1, 2, and 4. For axial locations beyond 10 hydraulic diameters, the Tollmien-Reichardt analysis for circular jets provides a good estimate of annular jet behavior. Furthermore, the pattern of an annular jet is independent of either the Reynolds number or the length-to-diameter ratio.

As has been recently pointed out by other investigators (Obot et al., 1984, 1986), much of the past work on free jets does not provide an adequate description of practical nozzles used in industry. This present paper concerns itself with the isothermal velocity fields issuing from annuli with sharp-edged inlets. An example of the industrial use of such a jet is the melt blowing process for producing microfibers (Shambaugh, 1988).

Many researchers have studied the behavior of free air jets. Taylor et al. (1951), Donald and Singer (1959), Wagnowski and Fiedler (1969), Donaldson et al. (1971), and Beltaos and Rajaratnam (1974) are only a few examples of the numerous publications on the experimental investigation of free jet characteristics. Most experimental work was done with short, convergent discharge nozzles. Only

Boguslawski and Popiel (1979) and Wall et al. (1980) studied the development of free jets issuing from long tubes. Obot et al. (1984, 1986), on the other hand, analyzed the flow fields of air jets issuing from straight, sharp-edged entrance orifice plates. In the melt blowing process, the air jets exit from the die head through very small, annular orifices with a sharp-edged entrance configuration. (For some common types of melt blowing dies, an annular configuration is an approximation of the actual die head; see Shambaugh (1988).) No data, however, were found on the characteristics of free jets issuing from this type of aperture. Consequently, an experimental program was started to study the flow fields of free air jets exiting from small, annular apertures with a sharp-edged entrance configuration. Three different orifice plates were used with