International Journal of Thermophysics, Vol. 7, No. 3, 1986

Comparison of the Critical Liquid Volume Fraction to Rectilinear-Diameter Methods for Prediction of the Critical Density of Ethylene and Oxygen[1]

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A comparison of the prediction of the critical density for ethylene and oxygen from available coexistence density values using three methods is presented. The conventional rectilinear diameter, the rectilinear diameter with an additional term to represent the postulated curvature near the critical point, and the critical liquid volume fraction were each utilized to predict critical density values for ethylene and oxygen. The correlating functions and fitted constants for the three techniques are given for different ranges of saturation density values. The accepted saturation lines for ethylene and oxygen calculated from new correlations of thermodynamic properties for these fluids were used in this study. The critical density of ethylene was predicted using coexistence density values from 220 to 230 K and from 220 to 282.34 K. Similarly, the critical density for oxygen was predicted using coexistence densities from 100 to 116 K, from 100 to 154.004 K, and from 100 to 154.571 K. Values of the critical density predicted using the three methods are compared with the accepted critical density values for these fluids. The ability of the three methods to predict accurate critical density values using saturation densities at temperatures removed from the critical point is assessed.

KEY WORDS: coexistence densities; critical density; ethylene; liquid volume fraction; oxygen; rectilinear diameter; phase equilibria; pure fluids.

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[1] Paper presented at the Ninth Symposium on Thermophysical Properties, June 24–27, 1985, Boulder, Colorado, U.S.A.

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1. INTRODUCTION

Historically, values of critical densities for pure fluids have been predicted by fitting a rectilinear diameter function to liquid–vapor coexistence data and then extrapolating the resulting equation to the critical point, as described in Ref. 1. A typical form of such a rectilinear diameter equation is

$$\rho_l + \rho_v = A + B(T_c - T) \tag{1}$$

where ρ_l is the saturated liquid density, ρ_v is the saturated vapor density, T is the temperature, and T_c is the critical-point temperature. The values of $A = 2\rho_c$ (twice the critical density) and B are determined by least-squares fitting.

The use of such an expression to describe data near the critical point has been discussed in the literature [2–4]. Evidence points to a curvature in the diameter in the critical region. A typical form which may be used to account for this curvature is

$$\rho_l + \rho_v = A + B(T_c - T) + C(T_c - T)^{(1-D)} \tag{2}$$

where $A = 2\rho_c$, and B, C, and D are constants to be determined. The value of D, expected to be less than 1 based upon theoretical considerations, provides an infinite slope or "hook" at the critical point. Equation (2) can also be used to represent coexistence data and extrapolated to the critical point to obtain a critical density.

Another candidate for predicting critical densities from coexistence data is the critical liquid volume fraction function [5–7]. The form of this function for representing coexistence data is derived below.

The liquid volume fraction at coexistence, X_{LV}, determined from a mass balance is

$$X_{LV} = (\rho_t - \rho_v)/(\rho_l - \rho_v) \tag{3}$$

where ρ_t is the total density. If the critical density ρ_c is substituted for ρ_t in Eq. (3), then the critical liquid volume fraction is

$$X_{LVC} = (\rho_c - \rho_v)/(\rho_l - \rho_v) \tag{4}$$

The scaled equations given by Green *et al.* [8],

$$\rho_l - \rho_c = B_{1l}\varepsilon^{\beta} + B_{2l}\varepsilon^{\phi} + B_{3l}\varepsilon^{\psi} + \cdots \tag{5}$$

$$\rho_v - \rho_c = B_{1v}\varepsilon^{\beta} + B_{2v}\varepsilon^{\phi} + B_{3v}\varepsilon^{\psi} + \cdots \tag{6}$$

where B_{il} and B_{iv} are constants and $\varepsilon = T_c - T$, with $\beta \cong 0.35$, $\phi \cong 1.0$ and $\psi > 1.0$, are substituted into Eq. (4) with the result,

$$X_{LVC} = \frac{-B_{1v} + \mathrm{TERMS}\ (\varepsilon^{\mathrm{EXP}>0})}{(B_{1l} - B_{1v}) + \mathrm{TERMS}\ (\varepsilon^{\mathrm{EXP}>0})} \tag{7}$$

For first-order symmetry (in the limit), $B_{1\mathrm{v}} = -B_{1l}$, therefore

$$\lim_{T \to T_\mathrm{c}} X_\mathrm{LVC} = (-B_{1\mathrm{v}})/(B_{1l} - B_{1\mathrm{v}}) = \tfrac{1}{2} \tag{8}$$

Substituting Eq. (8) into Eq. (7) results in (after division and truncation)

$$X_\mathrm{LVC} = (\rho_\mathrm{c} - \rho_\mathrm{v})/(\rho_l - \rho_\mathrm{v}) = (\tfrac{1}{2})[1 - B\varepsilon^C - D\varepsilon^E] \tag{9}$$

After some algebraic manipulation an expression for the diameter is obtained:

$$\rho_l + \rho_\mathrm{v} = A + B(T_\mathrm{c} - T)^C(\rho_l - \rho_\mathrm{v}) + D(T_\mathrm{c} - T)^E(\rho_l - \rho_\mathrm{v}) \tag{10}$$

where $A = 2\rho_\mathrm{c}$, and B, C, D, and E are constants to be determined. The expression is similar to Eqs. (1) and (2) except that the expression $(\rho_l - \rho_\mathrm{v})$ modifies the $(T_\mathrm{c} - T)$ terms. Another important difference is that the use of Eq. (10) is not an extrapolative method. Rather, it is an interpolative technique in that fitting data to Eq. (10) is really fitting Eq. (9) where the critical liquid volume fraction is known at the critical point; it is $(\frac{1}{2})$.

In this work, critical densities for ethylene and oxygen have been predicted using the two extrapolative techniques—the rectilinear diameter with and without curvature, Eqs. (1) and (2)—and an interpolative technique utilizing the critical liquid volume fraction, Eq. (10). Accepted data near and removed from the critical point for ethylene [9] and oxygen [10, 11] are used to predict critical densities. These values will be published as ancillary parts of new internationally accepted formulations in cooperation with the International Union of Pure and Applied Chemistry Thermodynamic Tables Project Centre. The quality of the fits to the coexistence data and calculated critical densities is presented. Appendix A contains the fitted constants for the diameter equations. In Appendix B are tables showing the accepted coexistence data for both ethylene and oxygen. These data predict a limit of $(\frac{1}{2})$ at the critical point for the critical liquid volume fraction utilizing published ρ_c values in Eq. (4). The slight scatter in the values of the fraction near the critical point is due to uncertainties in the experimental data.

2. PREDICTION OF CRITICAL DENSITIES

The various diameter equations have been used to represent coexistence data in roughly the upper third of the temperature range of liquid–vapor coexistence for ethylene and the upper half for oxygen. These range choices were arbitrary. (The triple points are 104 and 54.361 K for ethylene and oxygen, respectively.) Table I shows the quality of the various

Table I. Comparisons of Calculated and Accepted Values of $\rho_l + \rho_v$ for Ethylene, 220–282.34 K

Temperature (K) ($T_c = 282.3452$ K)	$\rho_l + \rho_v$ (mol · dm^{-3}) data	Deviations (%)		
		Straight rect. dia	Rect. dia. with "hook"	Critical liquid volume fraction
220	17.9694	-0.154	-0.039	-0.001
222	17.8782	-0.129	-0.030	-0.000
224	17.7873	-0.104	-0.022	-0.000
226	17.6966	-0.081	-0.014	0.000
228	17.6061	-0.058	-0.007	0.000
230	17.5159	-0.037	-0.001	0.000
232	17.4259	-0.017	0.005	0.001
234	17.3361	0.003	0.010	0.001
236	17.2466	0.020	0.015	0.001
238	17.1575	0.036	0.018	0.001
240	17.0686	0.051	0.021	0.001
242	16.9800	0.064	0.023	0.000
244	16.8917	0.075	0.025	0.000
246	16.8038	0.085	0.025	-0.000
248	16.7161	0.093	0.025	-0.000
250	16.6289	0.098	0.023	-0.001
252	16.5419	0.102	0.021	-0.001
254	16.4554	0.103	0.018	-0.001
256	16.3691	0.102	0.014	-0.001
258	16.2834	0.099	0.009	-0.002
260	16.1980	0.093	0.004	-0.002
262	16.1130	0.085	-0.002	-0.001
264	16.0284	0.074	-0.009	-0.001
266	15.9443	0.060	-0.016	0.000
268	15.8606	0.043	-0.023	0.001
270	15.7774	0.022	-0.030	0.002
272	15.6947	-0.001	-0.037	0.004
274	15.6127	-0.029	-0.044	0.004
276	15.5312	-0.062	-0.049	0.003
278	15.4505	-0.099	-0.051	-0.001
280	15.3703	-0.140	-0.044	-0.009
282	15.2847	-0.146	0.024	-0.004
282.2	15.2815	-0.130	0.051	0.006
282.34	15.2665	-0.123	0.069	0.001

fits for ethylene in the range from 220 to 282.34 K. Table II gives similar results from 100 to 154.004 K for oxygen, and Table III includes results using additional data from Weber [11] in the range from 154.104 to 154.571 K. All of the data utilized for ethylene are shown in Table I. For oxygen, data were used at one-degree intervals (except above 154 K). About half the data utilized are shown in Table II (28 points vs 53 used) and Table III (37 points vs 72 used).

The best fit is for the critical liquid volume fraction, while the rec-

Table II. Comparisons of Calculated and Accepted Values of $\rho_l + \rho_v$ for Oxygen, 100–154.004 K

Temperature (K) ($T_c = 154.581$ K)	$\rho_l + \rho_v$ ($\mathrm{mol \cdot dm^{-3}}$) data	Deviations (%)		
		Straight rect. dia.	Rect. dia. with "hook"	Critical liquid volume fraction
100	34.4218	−0.238	−0.077	0.009
102	34.1417	−0.192	−0.059	0.004
104	33.8625	−0.147	−0.041	0.001
106	33.5842	−0.104	−0.025	−0.002
108	33.3068	−0.063	−0.010	−0.003
110	33.0305	−0.026	0.004	−0.004
112	32.7553	0.010	0.016	−0.004
114	32.4812	0.042	0.027	−0.004
116	32.2084	0.072	0.036	−0.003
118	31.9370	0.097	0.042	−0.002
120	31.6669	0.118	0.047	−0.001
122	31.3983	0.136	0.049	−0.000
124	31.1312	0.148	0.049	0.001
126	30.8657	0.156	0.047	0.002
128	30.6019	0.158	0.042	0.003
130	30.3399	0.154	0.030	0.003
132	30.0798	0.144	0.024	0.003
134	29.8215	0.128	0.012	0.003
136	29.5653	0.105	−0.003	0.002
138	29.3109	0.074	−0.020	0.001
140	29.0586	0.036	−0.037	−0.000
142	28.8081	−0.008	−0.053	−0.001
144	28.5593	−0.060	−0.068	−0.001
146	28.3120	−0.118	−0.076	−0.000
148	28.0656	−0.180	−0.073	0.003
150	27.8252	−0.265	−0.071	−0.017
153.003	27.4511	−0.347	0.051	−0.017
154.004	27.3073	−0.305	0.210	−0.019

Table III. Comparisons of Calculated and Accepted Values of $\rho_l + \rho_v$ for Oxygen, 100–154.571 K

Temperature (K) ($T_c = 154.581$ K)	$\rho_l + \rho_v$ (mol · dm^{-3}) data	Deviations (%)		
		Straight rect. dia.	Rect. dia. with "hook"	Critical liquid volume fraction
100	34.4218	−0.322	−0.084	−0.001
102	34.1417	−0.267	−0.064	−0.003
104	33.8625	−0.213	−0.046	−0.003
106	33.5842	−0.161	−0.028	−0.003
108	33.3068	−0.111	−0.012	−0.002
110	33.0305	−0.063	0.003	−0.001
112	32.7553	−0.018	0.016	0.000
114	32.4812	0.024	0.028	0.002
116	32.2084	0.063	0.038	0.003
118	31.9370	0.099	0.046	0.004
120	31.6669	0.131	0.052	0.005
122	31.3983	0.158	0.056	0.005
124	31.1312	0.182	0.057	0.006
126	30.8657	0.200	0.055	0.005
128	30.6019	0.213	0.051	0.004
130	30.3399	0.221	0.044	0.003
132	30.0798	0.222	0.034	0.001
134	29.8215	0.218	0.021	−0.001
136	29.5653	0.206	0.005	−0.004
138	29.1845	0.188	−0.013	−0.007
140	29.0586	0.162	−0.033	−0.009
142	28.8081	0.130	−0.054	−0.011
144	28.5593	0.091	−0.074	−0.010
146	28.3120	0.046	−0.091	−0.007
148	28.0656	−0.003	−0.101	0.001
150	27.8252	−0.075	−0.118	−0.008
153.003	27.4511	−0.136	−0.050	0.025
153.504	27.3916	−0.158	−0.040	0.013
154.004	27.3073	−0.088	0.069	0.086
154.105	27.3072	−0.135	0.030	0.036
154.304	27.2792	−0.128	0.057	0.037
154.495	27.2854	−0.242	−0.035	−0.091
154.515	27.2666	−0.182	0.028	−0.035
154.545	27.2698	−0.208	0.006	−0.066
154.551	27.2698	−0.211	0.004	−0.071
154.571	27.3042	−0.347	−0.128	−0.212
154.571	27.2198	−0.038	0.182	0.099

tilinear diameter with curvature is an improvement on the straight-line form. Given that the critical liquid volume fraction was formed using scaling laws usually appropriate only in the critical region, the quality of fit is quite acceptable. Certainly, the fact that this is an interpolative technique has an important bearing on this result.

A further result of fitting Eqs. (1), (2), and (10) to coexistence data is an estimation of the critical density ($A/2$ in each case). These results are shown in Table IV for ethylene and Table V for oxygen. Comparisons to the accepted values are included.

For ethylene, when the entire range of data (220–282.34 K) is utilized, there is not a significant difference in the results from the various diameters. The diameter with curvature yields a slight improvement over the straight-line version. The critical liquid volume fraction yields the closest value of the critical density. The data show consistency with the thermodynamic criterion that the critical liquid volume fraction is ($\frac{1}{2}$) at the critical point. Equation (10) reflects this condition, indicating that the critical density predicted is consistent with proper behavior of the critical liquid volume fraction at the critical point.

The prediction of the critical density utilizing data removed from the critical region (where coexistence data are obtained only with some difficulty) is necessary for some fluids. To examine the effects of this procedure, data in a limited region (220–230 K) have been represented by the three diameters. The straight-line diameter and the one with curvature yield similar results. The constant D, which yields the curvature, did not take on values consistent with theory as shown in Appendix A. The data are too far removed from the critical regions for proper sensitivity to curvature. The diameter based on the critical liquid volume fraction does an acceptable job of prediction. Again, the interpolative character of this method has a probable bearing on this result.

Table IV. Comparisons of Predicted Critical Densities for Ethylene

Temperature range of data (K)	Published ρ_c (mol · dm^{-3})	Estimated ρ_c and deviation in %		
		Straight rect. dia.	Rect. dia. with "hook"	Critical liquid volume fraction
220–230	7.634	7.571 (–0.83)	7.572 (–0.82)	7.625 (–0.12)
220–282.34	7.634	7.624 (–0.13)	7.639 (0.06)	7.633 (–0.01)

Table V. Comparisons of Predicted Critical Densities for Oxygen

Temperature range of data (K)	Published ρ_c (mol · dm^{-3})	Estimated ρ_c and Deviation in % Straight rect. dia.	Rect. dia. with "hook"	Critical liquid volume fraction
100–116	13.630	13.432 (-1.45)	13.346 (-2.08)	13.622 (-0.06)
100–154.004	13.630	13.574 (-0.41)	13.662 (0.23)	13.603 (-0.16)
100–154.571	13.630	13.604 (-0.19)	13.634 (0.03)	13.622 (-0.06)

Similar results are shown for oxygen in Table V. When data in the critical region are utilized for oxygen, all three diameters give reasonable estimations of ρ_c. However, when data in a small range (100–116 K) quite removed from the critical point are utilized, the diameter based on the critical liquid volume fraction achieves significantly better results.

3. CONCLUSIONS

The interpolative method of the critical liquid volume fraction yields an excellent prediction of the critical density for all temperature ranges considered. The extrapolative technique using the rectilinear diameter with or without curvature achieves acceptable predictions of the critical density when data in the critical region are utilized. However, when data removed from this region are utilized, the prediction of the critical density is less accurate than that determined using the critical liquid volume fraction.

The probable reason for the success of the method using the diameter from the critical liquid volume fraction is that it contains within it information at the critical point ($X_{\text{LVC}} = \frac{1}{2}$). This allows a reasonable predictive accuracy even when data are available only at temperatures some distance below the critical temperature. Neither of the other diameters contains this information about the critical point.

APPENDIX A

Table AI. Fitted Constants in Equations for Various Diameters

Equation No.	A	B	C	D	E
			Ethylene, 220–230 K		
(1)	0.15141736×10^{2}	$0.45348272 \times 10^{-1}$	0.	0.	0.
(2)	0.15143105×10^{2}	$0.45347005 \times 10^{-1}$	$-0.26995133 \times 10^{-2}$	0.11828749×10^{1}	0.
(10)	0.15250349×10^{2}	$0.11663318 \times 10^{-1}$	0.49010869	$0.12106420 \times 10^{-2}$	0.99576571
			Ethylene 220–282.3452 K		
(1)	0.15247455×10^{2}	$0.43212444 \times 10^{-1}$	0.	0.	0.
(2)	0.15277013×10^{2}	$0.79750659 \times 10^{-1}$	$-0.44619588 \times 10^{-1}$	$0.47432896 \times 10^{-1}$	0.
(10)	0.15266196×10^{2}	$0.10588459 \times 10^{-1}$	0.52177155	$0.11577324 \times 10^{-2}$	0.99306671
			Oxygen 100–116 K		
(1)	0.26864754×10^{2}	0.13836454	0.	0.	0.
(2)	0.26692288×10^{2}	0.13919739	0.40760600	0.12907852×10^{1}	0.
(10)	0.27244841×10^{2}	$0.14303473 \times 10^{-1}$	0.52644320	$0.14479763 \times 10^{-2}$	0.10461924×10^{1}
			Oxygen 100–154.004 K		
(1)	0.27147912×10^{2}	0.13176424	0.	0.	0.
(2)	0.27323577×10^{2}	0.16221238	$-0.80391793 \times 10^{-1}$	0.22530186	0.
(10)	0.27215827×10^{2}	$0.17160887 \times 10^{-1}$	0.46705417	$0.13736667 \times 10^{-2}$	0.10777891×10^{1}
			Oxygen 100–154.571 K		
(1)	0.27208246×10^{2}	0.13013007	0.	0.	0.
(2)	0.27268684×10^{2}	0.28227049	−0.17875573	$0.40962021 \times 10^{-1}$	0.
(10)	0.27243968×10^{2}	$0.15465738 \times 10^{-1}$	0.49462471	$0.14845361 \times 10^{-2}$	0.10543643×10^{1}

APPENDIX B

Table BI. Calculation of Critical Liquid Volume Fraction for Ethylene

Temperature (K)	ρ_l (mol · dm^{-3})	ρ_v (mol · dm^3)	$X_{LVC} = (7.634 - \rho_v)/(\rho_l - \rho_v)$
220	17.3472	0.622174	0.4192
222	17.2132	0.665021	0.4211
224	17.0770	0.710286	0.4230
226	16.9385	0.758103	0.4250
228	16.7975	0.808619	0.4269
230	16.6539	0.861996	0.4288
232	16.5075	0.918408	0.4308
234	16.3581	0.978049	0.4328
236	16.2055	1.04113	0.4348
238	16.0496	1.11079	0.4368
240	15.8900	1.17859	0.4388
242	15.7265	1.25353	0.4409
244	15.5587	1.33303	0.4429
246	15.3863	1.41748	0.4450
248	15.2088	1.50730	0.4472
250	15.0259	1.60299	0.4493
252	14.8368	1.70512	0.4515
254	14.6410	1.81437	0.4537
256	14.4376	1.93154	0.4560
258	14.2258	2.05759	0.4583
260	14.0043	2.19370	0.4606
262	13.7717	2.34131	0.4630
264	13.5261	2.50227	0.4655
266	13.2653	2.67896	0.4681
268	12.9860	2.87458	0.4707
270	12.6839	3.09352	0.4734
272	12.3525	3.34219	0.4763
274	11.9822	3.63049	0.4794
276	11.5561	3.97515	0.4826
278	11.0417	4.40884	0.4862
280	10.3561	5.01418	0.4904
282	9.02541	6.25929	0.4970
282.2	8.67111	6.60255	0.4986
282.34	7.97796	7.28857	0.5011

Table BII. Calculation of Critical Liquid Volume Fraction for Oxygen

Temperature (K)	ρ_l $(\text{mol} \cdot \text{dm}^{-3})$	ρ_v $(\text{mol} \cdot \text{dm}^{-3})$	$X_{\text{LVC}} = (13.63 - \rho_v)/(\rho_l - \rho_v)$
100	34.0958	0.325962	0.3940
102	33.7618	0.379894	0.3969
104	33.4222	0.440286	0.3999
106	33.0765	0.507657	0.4029
108	32.7242	0.582566	0.4059
110	32.1823	0.665616	0.4090
112	31.9978	0.757466	0.4120
114	31.6224	0.858838	0.4151
116	31.2379	0.970539	0.4183
118	30.8435	1.09347	0.4214
120	30.4383	1.22864	0.4246
122	30.0211	1.37722	0.4278
124	29.5907	1.54053	0.4310
126	29.1456	1.72013	0.4343
128	28.6841	1.91785	0.4376
130	28.2041	2.13584	0.4409
132	27.7031	2.37672	0.4443
134	27.1778	2.64370	0.4478
136	26.6245	2.94076	0.4513
138	26.0379	3.27304	0.4550
140	25.4113	3.64727	0.4587
142	24.7354	4.07268	0.4625
144	23.9968	4.56248	0.4666
146	23.1751	5.13690	0.4708
148	22.2359	5.82968	0.4754
150	21.1093	6.71588	0.4804
153.003	18.6351	8.81596	0.4903
153.504	17.9819	9.40973	0.4923
154.004	17.0944	10.2129	0.4966
154.105	16.8631	10.4441	0.4963
154.304	16.2850	10.9942	0.4982
154.495	15.4006	11.8848	0.4964
154.515	15.2412	12.0254	0.4990
154.545	14.9318	12.3380	0.4981
154.551	14.8193	12.4505	0.4979
154.571	14.4287	12.8755	0.4858
154.571	14.4568	12.7630	0.5119

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