A Critical Evaluation of Methods for the Prediction of Critical Properties of Hydrocarbons

A critical evaluation and modification of the available methods for the estimation of critical properties of pure hydrocarbons was undertaken to determine the most accurate method which has general applicability with minimum input data. As a result of the study, the method of Nokay as modified by the authors is recommended for the estimation of critical temperature while the method of Reidel is the best general method for critical volume. For critical pressure the Lydersen method is preferred for saturated hydrocarbons, while the method of Forman and Thodos is somewhat better for unsaturated hydrocarbons.

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SCOPE

Critical properties are essential in estimating thermodynamic and volumetric properties by the theorem of corresponding states. They are also of importance in determining the existing phase conditions in or the permissible operating ranges of both reactors and mass transfer equipment. As critical properties are often difficult to measure experimentally, reliable methods for correlating and predicting them are necessary.

The major objective of this study was to evaluate critically and, if necessary, modify the available methods for the estimation of critical properties of pure hydrocarbons. Constraints on the study were that the method must be of general applicability for several families of compounds and that input parameters are normally available or easily obtained.

Although there is no critical and independent review of all available correlations in the current literature, this study has considered all general methods located not already rejected by previous investigators in line with the constraints given above.

CONCLUSIONS AND SIGNIFICANCE

As a result of this study the methods discussed below are proposed as the best available generalized techniques for estimating the critical properties of pure hydrocarbons.

For critical temperature, the method of Nokay (1959) [Equation (4)] which requires only the specific gravity and normal boiling point of the material together with the revised constants (A, B, and C listed in Table 5) is recommended for all chemical families. An average error of only 3.6 K ($<0.5\%$) should be expected in the prediction.

The methods of Lydersen (1955) [Equation (5)] and Forman-Thodos (1958, 1960) [Equation (6)] are recommended for the estimation of the critical pressure of saturated and unsaturated hydrocarbons, respectively. Average errors depending on the chemical family are 3 to 4%. Only the structure of the molecule is required in either method.

Critical volumes are best estimated by the method of Reidel (1954) [Equation (10)] using α calculated from Equation (11) for most chemical families with an average error of 2%. The critical temperature and pressure and the normal boiling point must be provided as input parameters. The method of Lydersen (1955) [Equation (7)] has a slight advantage for unsaturates.

The properties calculated by such methods are useful in their own right to estimate existing phase conditions. They also can be used to determine properties for hydrocarbons existing in mixtures prior to the use of correlations for true- and pseudo-critical properties necessary for phase equilibrium calculations and estimation of thermodynamic properties by the theorem of corresponding states.

PREVIOUS WORK

Correlational attempts on the critical properties of pure liquids are numerous and have been reviewed by several authors. Reid and Sherwood (1966), Ogle and Gold (1968), and Kudchadker et al. (1968a) present major reviews of the methods available, each with a detailed analysis of the methods evaluated. In general, each agrees that the Lydersen (1955) group-contribution method is relatively accurate and the most reliable for estimation of T_c, P_c, and V_c over the range of materials. Kudchadker et al. (1968a) separated the various classes of hydrocarbons into homologous series and recommended the best

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methods available for each. These included Kudchadker et al. (1968b) for isomeric paraffins, Lydersen (1955) for alkylcycloalkanes, Lydersen (1955) or Forman and Thodos (1958) for branched alkenes and alkynes, and Maslov (1960) for alkylbenzenes, together with other recommendations on other organics.

Correlations advanced since or not included in the reviews listed above are given along with the recommended correlations from these reviews in Tables 1, 2, and 3 of the following section.

SELECTION OF CORRELATIONS FOR EVALUATION

Based on the findings of past investigators, the addition of more recent correlations, and on the criterion that a useful method must have input parameters which are readily available and reasonably accurate, a selection of correlations for each critical property was made.

Tables 1, 2, and 3 list available correlations for critical temperature, pressure, and volume, respectively, together with the classes of hydrocarbons for which they apply. Only correlations which showed reasonable promise in past evaluations as well as more recent developments are included. The comments on accuracy noted in the tables are those of the proposers.

Certain methods were eliminated from evaluation because of their limited applicability or because they require input parameters which are difficult to measure or predict accurately in their own right. Thus, for critical temperature methods 1, 2, 3, and 4 of Table 1; for critical pressure methods 1 and 2 of Table 2, and for critical volume, methods 1, 2, 3, and 4 of Table 3 were evaluated.

DATA SOURCES

All data have been taken from API Research Project 44 (1971) tabulations. The authors will furnish a list of the data set on request.

TABLE 1. AVAILABLE CORRELATIONS FOR CRITICAL TEMPERATURE

Proposer	Class of hydrocarbon recommended for	Input parameters	Comments
1. Lydersen (1955)	Alkylcycloalkanes Branched alkenes Alkynes	1. T_b 2. Δ_T	1. Reports <2% error for 90% of compounds tested
Reidel (1963)	Branched alkanes		2. No differentiation between different compounds with the same skeletal group and normal boiling point
2. Forman and Thodos (1958, 1960)	Hydrocarbons	1. Structure of molecule	1. Report average error of 1%
3. Nokay (1959)	Hydrocarbons	1. Specific gravity 60/60 2. T_b 3. Three constants which vary with hydrocarbon family	
4. Mathur, Ibrahim, and Kuloor (1969)	Normal aliphatic hydrocarbons *n*-cycloparaffins *n*-alkylbenzenes	1. M 2. Two constants which vary with homologous series	1. Report average error of 0.8% 2. No allowance for geometric isomerism
5. Maslov (1960)	Alkylbenzenes	1. Structure of molecule	1. Reports average error of 1%
6. Kudchadker, Holcomb, and Zwolinski (1968)	Isomeric alkanes (C_4-C_8)	1. Molecular structure 2. T_b 3. T_b of normal alkane 4. T_c of normal alkane	1. Report average deviation of 0.07%

TABLE 2. AVAILABLE CORRELATIONS FOR CRITICAL PRESSURE

Proposer	Class of hydrocarbon recommended for	Input parameters	Comments
1. Lydersen (1955)	Alkylcycloalkanes Branched alkenes Alkynes	1. M 2. Δ_p	1. Reports average error of 3.8% 2. No correction for different compounds with same skeletal groups
Reidel (1963)	Branched alkanes		
2. Forman and Thodos (1958, 1960)	Hydrocarbons	1. Structure of molecule	1. Report average error of 2%
3. Hakuta and Hirata (1970)	All organics	1. T_c 2. T_b 3. *a* density 4. specific constant for each chemical family 5. V_c 6. ω or Z_c	1. Report average error of 2.4%
4. Maslov (1960)	Alkylbenzenes	1. Structure of molecule	1. Reports average error of 3%
5. Kudchadker, Holcomb, and Zwolinski (1968)	Isomeric alkanes (C_4-C_8)	1. Molecular structure 2. p_c of normal alkane	1. Report average deviation of 0.37%

TABLE 3. AVAILABLE CORRELATIONS FOR CRITICAL VOLUME

Proposer	Class of hydrocarbon recommended for	Input parameters	Comments
1. Lydersen (1955)	Alkylcycloalkanes Branched alkenes Alkynes	1. Δv	1. Reports average error of 2.3% 2. No correction for geometric isomerism
Reidel (1963)	Branched alkanes		
2. Riedel (1954)	All organics	1. T_c 2. p_c 3. T_b	1. No dependence on homologous series
3. Hall and Yarborough (1971)	Hydrocarbons	1. M 2. Specific Gravity 60/60	1. No dependence on homologous series
4. Viswanath (1968)	Organics	1. T_c 2. p_c	1. Reports average deviation of 1.6%
5. Maslov (1960)	Alkylbenzenes	1. Structure of molecule	1. Reports average error of 3%
6. Kudchadker, Holcomb, and Zwolinski (1968)	Isomeric alkanes (C_4-C_8)	1. Molecular structure 2. V_c of normal alkane	

TABLE 4. COMPARISON OF THE METHODS FOR PREDICTION OF CRITICAL TEMPERATURE

	Method								
	Mathur et al.		Forman-Thodos		Lydersen		Nokay		
							Avg. dev., K		
Chem. family	Avg. dev., K	Data points	Avg. dev., K	Data points	Avg. dev., K	Data points	Orig. constants	Revised constants	Data points
Paraffins	4.77	20	7.55	78	3.12	86	2.09	2.05	83
Naphthenes	11.00	27	8.24	35	8.32	36	6.16	5.03	36
Olefins	4.73	9	3.74	34	6.62	34	3.77	3.92	34
Diolefins	—	—	12.08	9	8.20	9	7.90	2.43	9
Acetylenes	18.07	7	9.18	14	8.10	14	15.84	6.65	14
Aromatics	5.56	5	7.01	24	5.20	26	17.13	4.79	26
Overall avg. dev.	8.66	68	7.27	194	5.44	205	6.25	3.58	202
Maximum deviation	28	—	32	—	18	—	19	19	—

Chemical Family	Number of Data Points T_c	P_c	V_c	Data Range
Paraffins	86	86	78	C_1-C_{20}
Naphthenes	36	35	6	C_3-C_{10}
Olefins	34	34	13	C_2-C_{10}
Diolefins	9	9	2	C_3-C_6
Acetylenes	14	14	5	C_2-C_8
Aromatics (mono and di)	26	24	22	C_6-C_{14}
Total	205	202	126	

CRITICAL TEMPERATURE

Lydersen (1955) described a group-contribution method for estimating critical temperature utilizing atomic and structural increments for each multivalent atom or group in the molecule. His final equation is

$$T_b/T_c = 0.567 + \Sigma\,\Delta_T - (\Sigma\Delta_T)^2 \tag{1}$$

where the Δ_T's are given by the author and by Reid and Sherwood (1966) for each group. Forman and Thodos (1958, 1960) devised a group contribution method which depends on structure and estimates suitable van der Waals' constants (a and b) which are correlated with molecular structure. Then the simple equation

$$T_c = 8a/27b\,R \tag{2}$$

can be used for estimation purposes. Values for the increments of a and b were given in the original paper and have been republished together with a detailed procedure by Reid and Sherwood (1966).

Mathur et al. (1969) developed a simple relationship which for hydrocarbons is

$$T_c = n_1\,(\log M) + C_1 \tag{3}$$

where n_1 and C_1 are specific constants for each different homologous series. Geometric isomerism is not considered.

Nokay (1959) has correlated critical temperature by

$$\log T_c = A + B \log\,(\text{Sp. Gr.}) + C \log T_b \tag{4}$$

where A, B, and C have been derived for each homologous series of compounds.

Results of the evaluations are summarized in Table 4. The method of Mathur et al. was the poorest of the correlations based on preliminary work and was eliminated. Nokay, Lydersen, and Forman-Thodos were almost equivalent in the first evaluation. As the Nokay method showed excellent results for saturates and olefins but poor correlations for more highly unsaturated compounds and for aromatics, a multiple least squares regression program was used to derive the new constants given in Table 5 improving the results markedly. This improved Nokay method is recommended for use on all classes of hydrocarbons.

CRITICAL PRESSURE

Lydersen's method (1955) for critical pressure again involves group contributions derived by the author and results in a simple equation

$$P_c = 0.101325\ M/(\Sigma\Delta p + 0.34)^2 \tag{5}$$

where Δp's are available for each group. Forman and

Thodos (1958, 1960) use the same parameters (a and b) as for critical temperature which result in the expression

$$P_c = 0.101325\ a/27b^2 \tag{6}$$

The results of these evaluations are given in Table 6. For saturated compounds and aromatics, the methods are essentially equivalent with Lydersen having the advantage because of its simplicity and slightly better accuracy. However, the Forman-Thodos method is appreciably better for all classes of unsaturated compounds and is recommended for these.

CRITICAL VOLUME

Lydersen (1955) advanced another group contribution method for critical volume which is simply

$$V_c = (2.497 + 0.06243\ \Sigma\Delta_v)/M \tag{7}$$

Viswanath (1968) estimated V_c from T_c and p_c by the simple equation

$$V_c = (0.6243 + 0.259\ RT_c/P_c)/M \tag{8}$$

Hall and Yarborough (1971) correlated critical volume with the equation

$$V_c = 0.001560 \left[\frac{M}{\text{Sp.Gr.}\ 0.69} \right]^{1.15} \tag{9}$$

Reidel (1954) proposed the following correlation for V_c

$$V_c = \frac{RT_c}{P_c} [3.72 + 0.26(\alpha - 7.0)]^{-1} \tag{10}$$

where

$$\alpha = 0.9076 \left[1.0 + \frac{(T_b/T_c) \ln P_c'}{1.0 - (T_b/T_c)} \right] \tag{11}$$

$$P_c' = P_c/1.01325\ (10^5)$$

Evaluation of the methods are summarized in Table 7 with the correlation of Reidel showing the greatest accuracy for saturates and aromatics with the correlation of Lydersen having a slight advantage for unsaturated hydrocarbons.

TABLE 5. SUMMARY OF REVISED CONSTANTS FOR USE IN NOKAY'S EQUATION FOR PREDICTING CRITICAL TEMPERATURE

Family of compounds	A	B	C
Alkanes (paraffins)	1.359397	0.436843	0.562244
Cycloalkanes (naphthenes)	0.658122	−0.071646	0.811961
Alkenes (olefins)	1.095340	0.277495	0.655628
Alkynes (acetylenes)	0.746733	0.303809	0.799872
Alkadienes (diolefins)	0.147578	−0.396178	0.994809
Aromatics	1.057019	0.227320	0.669286

TABLE 6. COMPARISON OF THE METHODS FOR PREDICTION OF CRITICAL PRESSURE

	Method			
	Lydersen		Forman-Thodos	
Chem. family	Avg. dev., MN/m^2	Data points	Avg. dev., MN/m^2	Data points
Paraffins	0.0949	86	0.0945	78
Naphthenes	0.1089	35	0.1401	35
Olefins	0.1159	34	0.0866	34
Diolefins	0.3233	9	0.0931	9
Acetylenes	0.2044	14	0.1435	14
Aromatics	0.1176	24	0.1326	24
Overall avg. dev.	0.1213	202	0.1096	194
Maximum deviation	0.60	—	0.65	—

TABLE 7. RESULTS OF THE EVALUATION OF METHODS FOR PREDICTING THE CRITICAL VOLUME OF PURE HYDROCARBONS

		Avg. deviation, $m^3/kg \times 10^3$			
Chemical family	No. of data points	Lydersen	Viswanath	Riedel	Hall-Yarborough
Paraffins	78	0.1205	0.1617	0.0868	0.1636
Naphthenes	6	0.0306	0.0606	0.0268	0.0643
Olefins	13	0.1673	0.1654	0.1785	0.2260
Diolefins	2	0.0537	0.0387	0.0581	0.1779
Acetylenes	5	0.0325	0.0755	0.0624	0.2628
Aromatics	22	0.0925	0.0874	0.0661	0.1105
Overall avg. dev.	126	0.1120	0.1386	0.0888	0.1607
Maximum deviation	—	0.62	0.70	0.67	0.99

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NOTATION

a = constant in Forman-Thodos correlations, cm^6 atm/(g mole)^2
b = constant in Forman-Thodos correlations, cm^3/g mole
A, B, C = constants in Nokay correlation
C_1 = constant in correlation of Mathur et al.
M = molecular weight
n_1 = constant in correlation of Mathur et al.
P_c = critical pressure, MN/m^2
R = gas constant
Sp. Gr. = specific gravity at 60°F (15.56°C)
T_b = normal boiling point, K
T_c = critical temperature, K
V_c = critical volume, m^3/kg

Greek Letters

α = Reidel factor defined by Equation (11)
Δ_p = Lydersen group contribution increments for P_c
Δ_T = Lydersen group contribution increments for T_c
Δ_V = Lydersen group contribution increments for V_c

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Computation of Three-Dimensional Viscous Flow Between Convergent Traveling Surfaces

The Marker-and-Cell numerical technique has been adapted to develop a method of solution for three-dimensional, unconfined, isothermal flow of a highly viscous, Newtonian fluid in a region bounded by two, nonparallel traveling surfaces. Results are reported only for plane and elliptical surfaces, but the analysis is general enough to handle any shape of interest.

A computer program was developed which can be used to generate and plot the flow and pressure fields. Numerical results were obtained for the special case of symmetrically opposed convergent surfaces for a wide range of conditions.

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SCOPE

A computer program was developed for prediction of the transient and steady flow of a highly viscous fluid between two wide, symmetrically opposed traveling surfaces. This method of forming plastic sheet is asserted by Bortnick et al. (1970) to be superior to the conventional system of fixed extruder die and takeoff rollers. The fluid is introduced between the moving surfaces as a jet as indicated in Figure 1. It undergoes changes in pressure and velocity that are governed by the volumetric rate of flow, the properties of the fluid, and the vertical spacing, velocity, and curvature of the traveling surfaces. The fluid is assumed to be Newtonian, incompressible, and isothermal.

The distinguishing characteristics of this process are the free boundaries of the fluid and the three-dimensionality. The process is described in terms of a mathematical model which is based on the general differential equations for the conservation of mass and momentum. A functional dependence is postulated for the variation of the velocity components in the vertical direction, and the resulting two-dimensional equations are solved numerically in the unsteady state using a modified form of the Marker-and-Cell method to keep track of the boundaries of the fluid. This is one of the most complex problems of flow that has yet been solved. It involves complexities not previously encountered with the Marker-and-Cell method. Hence the development of the general method of solution is described in considerable detail. The finite-difference representation which is more conventional is not described in detail.

The objective of the study has been to develop a method for prediction of the behavior of polymer melts during the forming of sheets. The investigation covers a range of flow conditions of practical interest and two configurations for the traveling surface.

CONCLUSIONS AND SIGNIFICANCE

Results in the form of tabulations and plots of the transient velocity and pressure fields were obtained directly from the computer. Typical results for two representative cases, one for convergent surfaces and the other for elliptical convergent surfaces, are presented in Figures 5 to 16. The conditions for these two cases are summarized in Table 2. Figure 5 shows the location of fluid particles at a series of times for the first case. Such plots could be projected in sequence to simulate the motion of the fluid. The location of the free boundary at a series of times

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