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Recommended Critical Pressures. Part I. Aliphatic Hydrocarbons

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This study presents 95 recommended experimental and 180 calculated values of critical pressures for saturated and unsaturated aliphatic hydrocarbons. This is the third article in a series dealing with recommended critical data for organic compounds. Previously critically evaluated data on normal boiling temperatures based on recommended experimental data base is also given in this study. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2201061]

Key words: alkanes; alkenes; critical pressure; evaluation; normal boiling points; prediction; recommended data.

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1. Introduction

Accurate evaluation of pure-substance critical parameters is essential for any calculations in multicomponent mixtures

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and further for many industrial processes designed. Critical constants have been experimentally determined for a limited number of compounds, as the decomposition processes and the necessity of obtaining accurate measurements in extreme conditions of high temperature and pressure constitute the main obstacle in the measurement process. In this case, prediction methods are the only means by which those properties may be determined.

This work is the third part of a general study of determination of critical parameters of the main groups of chemical compounds for which experimental data are not available in world literature. Two previous papers were concerned with the critical temperatures for aliphatic hydrocarbons Part I[1] and the critical temperatures for aromatic and cyclic hydrocarbons Part II.[2]

The main purpose of this work was the creation of recommended experimental critical pressure (P_c) data base for aliphatic hydrocarbons, as well as filling the existing lack of P_c values, as far as possible, by means of predictive methods.

The preliminary stages of this work were:

(a) Creation of a recommended experimental data base of P_c values of aliphatic hydrocarbons, named "test substances" for which the satisfactory quantity of experimental data has been found (Table 1). This data base was next used for evaluation of chosen methods.
(b) Comparative determination of the accuracy of individual predictive methods of calculation of critical pressure P_c values for hydrocarbons according to their different molecular structures; and the final aim was
(c) Application of the chosen predictive methods for determination of P_c values for aliphatic hydrocarbons for which the experimental data were not available in world literature.

The prediction methods for critical pressures require reliable and accurate values of normal boiling points T_b. Values of T_b needed for test substances as well as for those for which P_c values were calculated were taken from the set of recommended data for normal boiling points presented in Part I[1] of this series. For several substances, not mentioned in Part I[1], and for those for which more reliable experimental data have been found—the recommended T_b data base was created according to the rules described further in point 3 and in Part I.[1]

The experimental data were critically evaluated and statistically examined with the aim of choosing the most reliable P_c values for recommended data sets, mentioned in point (a). For evaluation purpose, mentioned in (b), the set of test substances was split into subgroups in order to determine if trends of deviations were reasonable.

Evaluation of applicability of prediction methods was effected by determining the dependence of their accuracy upon:

(1) a number of carbon atoms in a molecule,
(2) a number of substituted CH_3 groups,
(3) C_s/C_m ratio, where C_s is a general number of C atoms in side chains, and C_m is a number of C atoms in the main chain, and
(4) type of C–C bond.

A new method of prediction of critical parameters has been tested in this study—the method of Marrero–Gani.[9,10]

2. Description of Selected Methods of P_c Prediction

The following methods defined by their authors' names have been chosen for testing purposes as a result of a review and a critical analysis of the main prediction methods of P_c available in the literature: (1) Ambrose,[3] (2) Joback,[4] (3) Somayajulu,[5] (4) Jalowka-Daubert,[6,7] (5) Constantinou,[8] and (6) Marrero–Gani.[9,10]

The representation by most of these methods[1,4–8] is based on experimental data available up to 1979, 1984–1989, and 1994, respectively. Only Marrero–Gani[9,10] (2001) used more updated data. The experimental database, used for this study purpose, is being permanently updated up to 2005.

All tested methods of prediction of critical pressures employ group contribution techniques which determine correction factors for specific groups of atoms composing a molecule of a compound considered. Values of these factors (Δp) are tabulated for every method and their sum $\Delta P = \Sigma n_i \Delta p_i$ represents the final correction applied to the calculation of critical pressure. Particular methods differ among themselves by various group definitions. Most of them require the knowledge of:

(1) group contribution models based on molecular structure, and
(2) molecular weight.

The method of Jalowka–Daubert,[6,7] unlike the rest of the methods considered, requires additionally knowing:

(1) normal boiling point temperature, and
(2) critical temperature.

Investigated methods represent two distinctive classes:

(1) The first order group techniques which determine the molecule by means of simple group contribution, neglecting the next-nearest neighbors effects. Ambrose,[3] Joback,[4] and Somayajulu[5] methods belong to this class.
(2) The second order group techniques, which additionally take into consideration the influence of first- and second-level neighbors of a considered group. The Jalowka–Daubert,[6,7] Constantinou,[8] and Marrero–Gani[9,10] methods belong to this class.

In the short description of investigated methods provided below the following symbols are used: P_c=critical pressure (MPa); T_c=critical temperature (K); T_b=normal boiling point (K); Δp=contributions of single atoms or groups of atoms (tabulated[3–12]) compose a molecule; M=molecular weight; n_i=number of occurrences of group i.

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TABLE 1. Recommended experimental values of normal boiling points T_b (taken from Part I[1]) and critical pressures P_c for hydrocarbons, used in this work for testing the applied prediction methods

Formula	Name of compound	CAS RN	T_b (K)	P_c (kPa)
		Unbranched alkanes		
CH_4	methane	74-82-8	111.63	4600[13]
C_2H_6	ethane	74-84-0	184.55	4879[14]
C_3H_8	propane	74-98-6	231.05	4260[14]
C_4H_{10}	butane	106-97-8	272.70	3793[14]
C_5H_{12}	pentane	109-66-0	309.21	3370[14]
C_6H_{14}	hexane	110-54-3	341.88	2990[14]
C_7H_{16}	heptane	142-82-5	371.57	2730[14]
C_8H_{18}	octane	111-65-9	398.82	2490[14]
C_9H_{20}	nonane	111-84-2	423.96	2280[14]
$C_{10}H_{22}$	decane	124-18-5	447.30	2110[14]
$C_{11}H_{24}$	undecane	1120-21-4	469.08	2008[14]
$C_{12}H_{26}$	dodecane	112-40-3	489.47	1820[14]
$C_{13}H_{28}$	tridecane	629-50-5	508.60	1680[14]
$C_{14}H_{30}$	tetradecane	629-59-4	526.70	1570[14]
$C_{15}H_{32}$	pentadecane	629-62-9	543.83	1480[14]
$C_{16}H_{34}$	hexadecane	544-76-3	560.01	1400[14]
$C_{17}H_{36}$	heptadecane	629-78-7	574.25	1340[14]
$C_{18}H_{38}$	octadecane	593-45-3	590.22	1290[14]
$C_{19}H_{40}$	nonadecane	629-92-5	603.00	1160[14]
$C_{20}H_{42}$	eicosane	112-95-8	617.00	1080[14]
$C_{21}H_{44}$	heneicosane	629-94-7	636.05	1030[14]
$C_{22}H_{46}$	docosane	629-97-0	641.80	991[14]
$C_{23}H_{48}$	tricosane	638-67-5	653.30[a]	915[14b]
$C_{24}H_{50}$	tetracosane	646-31-1	664.50[a]	866[14b]
$C_{27}H_{56}$	heptacosane	593-49-7	695.4[a]	795[14b]
$C_{28}H_{58}$	octacosane	630-02-4	704.80[a]	744[14b]
		Branched alkanes		
C_4H_{10}	2-methylpropane	75-28-5	261.42	3650[14]
C_5H_{12}	2-methylbutane	78-78-4	301.00	3380[14]
C_5H_{12}	2,2-dimethylpropane	463-82-1	282.65	3196[14]
C_6H_{14}	2-methylpentane	107-83-5	333.41	3032[14]
C_6H_{14}	3-methylpentane	96-14-0	336.41	3124[14]
C_6H_{14}	2,2-dimethylbutane	75-83-2	322.88	3102[14]
C_6H_{14}	2,3-dimethylbutane	79-29-8	331.15	3145[14]
C_7H_{16}	2-methylhexane	591-76-4	363.15	2750[13]
C_7H_{16}	3-methylhexane	589-34-4	364.99	2813[14]
C_7H_{16}	3-ethylpentane	617-78-7	366.64	2891[13]
C_7H_{16}	2,2-dimethylpentane	590-35-2	352.35	2773[14]
C_7H_{16}	2,3-dimethylpentane	565-59-3	362.93	2908[14]
C_7H_{16}	2,4-dimethylpentane	108-08-7	353.66	2736[14]
C_7H_{16}	3,3-dimethylpentane	562-49-2	359.21	2946[14b]
C_7H_{16}	2,2,3-trimethylbutane	464-06-2	354.00	2953[14]
C_8H_{18}	2-methylheptane	592-27-8	390.80	2500[13]
C_8H_{18}	3-methylheptane	589-81-1	392.09	2550[14b]
C_8H_{18}	4-methylheptane	589-53-7	390.87	2542[14b]
C_8H_{18}	3-ethylhexane	619-99-8	391.70	2610[14b]
C_8H_{18}	2,2-dimethylhexane	590-73-8	380.00	2530[14b]
C_8H_{18}	3,3-dimethylhexane	563-16-6	385.81	2653[14b]
C_8H_{18}	3,4-dimethylhexane	583-48-2	390.88	2692[14b]
C_8H_{18}	2,3-dimethylhexane	584-94-1	388.76	2630[14b]
C_8H_{18}	2,4-dimethylhexane	589-43-5	382.58	2556[14b]
C_8H_{18}	2,5-dimethylhexane	592-13-2	382.27	2488[14b]
C_8H_{18}	2-methyl-3ethylpentane	609-26-7	388.80	2700[14b]
C_8H_{18}	3-methyl-3ethylpentane	1067-08-9	391.43	2807[14b]
C_8H_{18}	2,2,3-trimethylpentane	564-02-3	383.00	2730[14b]
C_8H_{18}	2,2,4-trimethylpentane	540-84-1	372.38	2568[14]

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TABLE 1. Recommended experimental values of normal boiling points T_b (taken from Part I[1]) and critical pressures P_c for hydrocarbons, used in this work for testing the applied prediction methods—Continued

Formula	Name of compound	CAS RN	T_b (K)	P_c (kPa)
C_8H_{18}	2,3,3-trimethylpentane	560-21-4	387.92	2820[14b]
C_8H_{18}	2,3,4-trimethylpentane	565-75-3	386.62	2730[14b]
C_8H_{18}	2,2,3,3-tetramethylbutane	594-82-1	379.65	2870[14]
C_8H_{20}	2-methyloctane	3221-61-2	416.43	2310[14]
C_8H_{20}	2,2-dimethylheptane	1071-26-7	405.99	2349[14b]
C_9H_{20}	2,2,3,3-tetramethylpentane	7154-79-2	413.42	2740[13]
C_9H_{20}	2,2,3,4-tetramethylpentane	1186-53-4	406.16	2602[14]
C_9H_{20}	2,2,4,4-tetramethylpentane	1070-87-7	395.43	2480[13]
C_9H_{20}	2,3,3,4-tetramethylpentane	16747-38-9	414.70	2720[13]
$C_{10}H_{22}$	3,3,5-trimethylheptane	7154-80-5	428.85	2320[13]
$C_{10}H_{22}$	2,2,5,5-tetramethylhexane	1071-81-4	410.61	2190[13b]
$C_{10}H_{22}$	2,2,3,3-tetramethylhexane	13475-81-5	433.46	2510[13b]
$C_{16}H_{34}$	2,2,4,4,6,8,8-heptamethylnonane	4930-04-9	519.5[a]	1570[14b]
	Alkenes, Alkynes			
C_2H_2	ethyne	74-86-2	189.55	6138[14]
C_2H_4	ethylene	74-85-1	169.25	5060[13]
C_3H_4	1-propyne	74-99-7	249.92	5628[13b]
C_3H_6	1-propene	115-07-1	225.45	4594[14]
C_4H_6	1-butyne	107-00-6	281.25	4586[14b]
C_4H_6	1,3-butadiene	106-99-0	268.75	4322[14b]
C_4H_8	*trans*-2-butene	624-64-6	274.01	3985[14]
C_4H_8	*cis*-2-butene	590-18-1	276.82	4245[14]
C_4H_8	1-butene	106-98-9	266.87	4023[14]
C_4H_8	2-methylpropene	115-11-7	266.22	4002[14]
C_5H_{10}	*cis*-2,pentene	627-20-3	309.78	3690[14b]
C_5H_{10}	*trans*-2,pentene	646-04-8	309.49[a]	3520[14]
C_5H_{10}	3-methyl-1-butene	563-45-1	293.35	3527[14b]
C_5H_{10}	2-methyl-1-butene	563-46-2	304.30	3850[14]
C_5H_{10}	2-methyl,2-butene	513-35-9	311.72	3415[14]
C_5H_{10}	1-pentene	109-67-1	303.15	3592[14]
C_6H_{12}	1-hexene	592-41-6	336.64	3212[14]
C_7H_{14}	1-heptene	592-76-7	366.80	2921[14b]
C_8H_{16}	1-octene	111-66-0	394.41	2675[14]
$C_{10}H_{20}$	1-decene	872-05-9	443.75	2218[14b]
$C_{12}H_{24}$	1-dodecene	112-41-4	486.55	1930[14b]
$C_{13}H_{26}$	1-tridecene	2437-56-1	505.99[a,b]	1730[14b]
$C_{14}H_{28}$	1-tetradecene	1120-36-1	524.32[a,b]	1590[14b]
$C_{15}H_{30}$	1-pentadecene	13360-61-7	541.61[a,b]	1540[14b]
$C_{16}H_{22}$	1-hexadecene	629-73-2	558.02[a,b]	1390[14b]
$C_{18}H_{36}$	1-octadecene	112-88-9	588.08[a,b]	1300[14b]
$C_{20}H_{40}$	1-eicosene	3452-07-1	617.20[a,b]	1140[14b]

[a]Values obtained in present study.
[b]Values from a single investigation.

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2.1. Ambrose's Method

Critical pressure is calculated as[3]

$$P_c = M\left(0.339 + \sum n_i \Delta p_i\right)^{-2}$$

where 0.339 is a dimensionless regression constant.

The value $\Sigma n_i \Delta p_i$ is evaluated by summing contributions Δp_i for atoms or groups of atoms. The branching is taken into consideration here by the correction factor called the delta Platt number, used only for branched alkanes.[3] The delta Platt number is evaluated on the basis of branch structure and included in $\Sigma \Delta p_i$ calculation as the n_i factor multiplied by the specific Platt correction factor Δp_i, tabulated together with Δp values.

2.2. Joback's Method

This is Joback's modification[4] of the Lydersen[11] method. The proposed formula for critical pressure is defined as:

$$P_c = \left(0.113 + 0.0032 n_a - \sum n_i \Delta p_i\right)^{-2}$$

where 0.113 and 0.0032 are dimensionless regression constants; and n_a is the number of atoms in the molecule.

2.3. Somayajulu's Method

This method[5] is comprised of procedures provided by the method developed by Kreglewski[12] for the calculation of critical constants of a homologous series of compounds. The proposed formula for T_c calculation is expressed as:

$$P_c = \frac{M}{G_p^2},$$

$$Gp = a_p + b_p \Delta P, \quad \Delta P = \sum n_i \Delta p_i$$

where: $a_p = 0.339$ and $b_p = 0.226$ constants, recorded in the Somayajulu[5] paper, ΔP is obtained by summation of the relevant group contribution indices Δp_i, listed by Somayajulu,[5] and Δp_i is pressure index of chosen group X, where $X = \Delta p(x)/\Delta p(-CH_3)$.

The gauche position factor (taking into consideration the degree of branching) for branched alkanes was introduced in this method as an element of Δp tabulated values.

2.4. Jalowka–Daubert's Method

This method employs normal boiling point, critical temperature, and contribution increments Δp.[6,7] Every type of compound is represented by a number of various groups describing in detail its molecular structure.

Jalowka and Daubert introduced second order groups, taking into account next-nearest neighbors effects. The central carbon atom of the group listed first is followed by a bond which indicates the ligands it is bonded to. All monovalent ligands are then listed followed by any other polyvalent ligands. A *cis*-correction group, treated as a Δp element, is introduced to take care of isomerization in alkene compounds. The functional form of the proposed model for P_c is expressed as:

$$P_c = \frac{T_c^3}{T_b^2\left(a_1 + \sum n_i \Delta p_i\right)}$$

where $a_1 = 43.387$ K/MPa is a regression constant; T_c = critical temperature (K); and T_b = normal boiling temperature.

2.5. Constantinou's Method

Estimation of critical parameters is performed at two levels.[8] The basic level uses contributions from first-order groups while the next higher level uses a small set of second-order groups having the first-order groups as building blocks. This method provides both first-order group contributions and more accurate second-order prediction for determination of the $\Sigma\Delta p$ pressure correction factor. Conjugation operators have been introduced in this method. It means that the molecular structure of a compound is viewed as a hybrid of a number of conjugate forms (alternative formal arrangements of valence electrons) and the property of a compound is a linear combination of this conjugate form contribution. Proposed correlation can be expressed as:

$$f(P_c) = \sum_i N_i C_i + W \sum_j M_j D_j$$

where $f(P_c) = (P_c - p_{c1})^{-0.5} - p_{c2}$, where p_{c1} and p_{c2} are universal constants, equal to 1.3705 bar and 0.100220 bar$^{-0.5}$, respectively; P_c is estimated critical pressure of a compound; C_i = the contribution of the first-order group of type i which occurs N_i times in a compound; D_j = the contribution of the second-order group of type j that occurs M_j times in a compound; and W = constant assigned to unity in the second level estimation, where both first- and second-order group contributions are involved; and 0 in the basic level, where only the contributions of first-order groups are employed.

2.6. Marrero–Gani's Method

This is the newest contribution method,[9,10] where estimation of critical parameters is performed at three levels. The primary level uses contributions from simple groups that allow describing a wide variety of organic compounds and provide an initial approximation that is improved at the higher levels. The higher levels involve polyfunctional and structural groups that provide more information about molecular fragments whose description through first-order groups is not possible.

The critical pressure estimation model has the form of the following equation:

$$f(P_c) = \sum_i N_i P_{c1i} + w \sum_j M_j P_{c2j} + z \sum_k O_k P_{c3k}$$

where: P_{c1i} is the contribution of the first-order group of type i that occurs N_i times; P_{c2i} is the contribution of the second-order group of type j that occurs M_j times and P_{c3k} is the contribution of the third-order group of type k that has O_k occurrences in a compound. $f(P_c) = (P_c - P_{c1})^{-0.5} - P_{c2}$ where P_{c1} and P_{c2} are the universal constants equal to 5.9827 bar and 0.108998 bar$^{-0.5}$, respectively.

3. Recommended Experimental Data on Normal Boiling Points and Critical Pressures

3.1. The Criterion and the Procedure for Selection of Experimental Data

The database of the recommended normal boiling point T_b and critical pressure P_c values for aliphatic hydrocarbons is based on all available experimental data extracted from the data banks in the frame of: Thermodynamics Research Center (NIST-TRC)[13] and Thermodynamics Data Center (TDC)[14] with the newest publications on P_c, as in numerous studies.[5,15–28]

The data references, attached to every experiment result, allowed us to judge whether specific data are the primary data (that is values were derived from the original observation) and let us know which method and equipment was used in the considered experiment. The short description, attached to every experiment result permitted us to know if the mea-

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TABLE 2. Deviations E (%) of predicted critical pressures from recommended experimental values for tested methods

	E (%) Author's name of method					
Name of compound	Ambrose	Joback	Somayajulu	Daubert	Constantinou	Marrero–Gani
			Unbranched alkanes			
methane	+17.96	+28.24	+9.24	+4.28	+53.63	+46.50
ethane	+0.35	+3.09	−1.50	−3.53	+0.02	+8.12
propane	+0.07	+3.50	+0.07	−1.41	+7.21	−2.44
butane	−0.82	+2.74	−0.82	−0.18	+5.14	+3.53
pentane	−0.80	+2.91	−0.80	+1.31	+4.69	+2.73
hexane	+0.33	+3.91	+0.33	+3.41	+5.25	+3.28
heptane	−0.55	+2.53	−0.55	+2.89	+3.55	+1.94
octane	−0.48	+1.81	−0.48	+2.85	+2.61	+1.61
nonane	−0.09	+1.18	−0.13	+2.72	+1.84	+1.71
decane	−0.19	−0.09	−0.19	+1.80	+0.52	+1.47
undecane	−2.44	−3.69	−2.44	−1.69	−3.04	−0.95
dodecane	+0.55	−2.20	+5.71	−0.11	−1.37	+2.09
tridecane	+2.20	−2.14	+2.20	−0.24	−1.13	+3.87
tetradecane	+6.43	−2.99	+2.99	−1.34	−1.72	+4.90
pentadecane	+3.24	−4.39	+3.18	−3.18	−2.84	+5.47
hexadecane	+3.43	−5.86	+3.43	−5.21	−4.00	+6.07
heptadecane	+2.69	−8.13	+2.69	−8.66	−8.73	−5.97
octadecane	+1.55	−10.70	+1.55	−11.47	−8.14	+5.19
nonadecane	+7.84	−6.81	+7.84	−9.05	−3.71	+12.41
eicosane	+10.83	−5.93	+10.83	−8.98	−2.31	+16.20
heneicosane	+11.36	−7.18	+11.36	−8.93	−3.01	+17.67
docosane	+11.10	−8.98	+11.10	−14.33	−4.34	+18.37
tricosane	+15.74	−6.89	+15.74	−13.77	−1.53	+24.26
tetracosane	+17.78	−6.93	+17.78	−15.24	−0.92	+27.60
heptacosane	+15.47	−13.33	+15.47	−25.79	−5.66	+28.81
octacosane	+19.35	−11.96	+19.35	−26.34	−3.36	+34.54
			Branched alkanes			
2-methylpropane	+3.78	+7.84	+0.16	+2.25	+8.49	+8.38
2-methylbutane	−0.27	+3.58	+0.59	+1.15	+3.37	+3.11
2,2-dimethylpropane	+9.01	+10.98	+1.35	+4.38	+11.48	+10.14
2-methylpentane	−0.33	+3.40	+0.36	+1.81	+3.17	+2.47
3-methylpentane	−0.26	+0.35	+0.99	+0.26	+0.64	−0.19
2,2-dimethylbutane	+0.23	+2.32	+1.00	+0.81	+2.39	+1.06
2,3-dimethylbutane	−0.19	+0.57	−1.81	+1.02	−1.14	−0.64
2-methylhexane	−0.65	+2.65	−0.00	+1.93	+2.18	+1.75
3-methylhexane	−0.18	+0.36	+0.92	+0.50	+0.39	−0.18
3-ethylpentane	−0.14	−2.35	+1.42	−1.49	−2.32	−2.87
2,2-dimethylpentane	+1.05	+3.03	+1.77	+1.98	+2.81	+1.73
2,3-dimethylpentane	−0.07	−2.10	−1.10	−0.10	−1.20	−0.17
2,4-dimethylpentane	+0.51	+4.06	+1.83	+1.72	+2.12	+2.81
3,3-dimethylpentane	+0.58	3.02	+2.21	−0.88	−1.87	−4.01
2,2,3-trimethylbutane	+0.98	−2.44	+3.35	+0.20	−4.03	−3.93
2-methylheptane	−0.32	+2.24	+0.28	+2.32	+1.64	+1.72
3-methylheptane	+0.16	+0.24	+1.14	+0.90	+0.08	+0.04
4-methylheptane	+0.47	+0.55	+1.46	+0.67	+0.39	+0.35
3-ethylhexane	+0.31	−2.07	+1.69	−1.57	−2.22	−2.26
2,2-dimethylhexane	+0.75	+2.17	+1.38	+1.82	+1.78	+1.26
3,3-dimethylhexane	+0.98	−2.56	−1.36	−0.30	−1.62	−3.20
3,4-dimethylhexane	+0.30	−4.27	−0.26	−1.56	−3.64	−2.30
2,3-dimethylhexane	+0.11	−2.02	−0.80	−0.19	−1.37	0.00
2,4-dimethylhexane	+0.47	+0.82	+2.07	−0.08	−0.70	+0.31
2,5-dimethylhexane	+0.72	+3.58	+1.89	+2.49	+1.57	+2.73

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TABLE 2. Deviations E (%) of predicted critical pressures from recommended experimental values for tested methods—Continued

	E (%) Author's name of method					
Name of compound	Ambrose	Joback	Somayajulu	Daubert	Constantinou	Marrero–Gani
2-methyl-3-ethylpentane	−0.00	−4.56	−0.45	−2.74	−0.81	+1.30
3-methyl-3-ethylpentane	+0.43	−7.91	−0.29	−3.42	−7.02	−8.51
2,2,3-trimethylpentane	+1.25	−4.54	+0.73	−0.92	−5.75	−5.38
2,2,4-trimethylpentane	−0.19	+1.48	+1.05	+0.47	−0.27	+0.27
2,3,3-trimethylpentane	+0.57	−7.59	+0.46	−1.99	−2.84	−2.34
2,3,4-trimethylpentane	−0.55	−4.84	−3.33	−1.36	−3.41	−0.62
2-methyloctane	−0.91	+0.65	−0.39	+1.43	−0.00	+0.87
2.2-dimethylheptane	−0.55	+0.04	+0.04	+0.43	+0.43	−0.21
2,2,3,3-tetramethylpentane	+0.62	−12.63	−1.46	−3.18	−0.15	−21.39
2,2,3,4-tetramethylpentane	−0.61	−8.26	−2.81	−2.92	−8.76	−6.57
2,2,4,4-tetramethylpentane	−3.35	−3.47	−2.22	−0.81	−4.92	−4.31
2,3,3,4-tetramethylpentane	−0.33	−12.24	+0.91	−3.79	+9.30	+7.38
3,3,5-trimethylheptane	−0.69	−6.85	+1.34	−2.33	−6.90	−5.91
2,2,5,5-tetramethylhexane	+0.78	−0.27	+1.83	−1.14	−0.55	−0.14
2,2,3,3-tetramethylhexane	−0.16	−12.99	−2.03	−4.94	−1.31	−20.32
2,2,4,4,6,8,8-heptamethylnonane	+0.89	−11.91	+2.93	−8.92	−12.29	−2.99
			Alkenes, Alkynes			
ethyne	+10.00	+0.37	+0.13	−1.56	−1.17	+5.02
ethylene	+5.18	+4.07	−0.32	+0.04	—	—
1-propyne	−0.76	−3.64	+0.18	+2.49	0.00	−0.78
1-propene	+1.07	+1.57	+1.68	−1.18	+6.57	+5.70
1-butyne	+2.44	+3.14	+3.23	+2.44	+5.97	+3.60
1,3-butadiene	+1.04	+0.42	+2.06	+0.02	+0.19	+2.98
1-butene	+0.50	+2.14	+0.99	+0.10	+1.44	+4.10
2-methylpropene	+1.02	+1.12	+1.52	−3.17	−1.55	+4.14
trans-2-butene	+1.46	+4.44	+0.03	+2.26	+4.34	+2.74
cis-2-butene	−4.76	−1.96	−0.52	−0.64	−2.05	−3.56
cis-2, pentene	3.58	+0.03	−0.00	+0.08	−0.57	−2.57
3-methyl-1-butene	+1.76	+4.39	−1.25	+1.16	−0.31	+4.42
trans-2-pentene	+1.08	+4.86	−0.14	+2.93	+4.23	+2.13
2-methyl-1-butene	−7.58	−4.70	−7.22	−8.91	−9.38	−5.01
2-methyl,2-butene	+4.19	+8.73	+8.05	+4.16	+2.61	+3.69
1-pentene	−0.95	+1.53	−0.56	−0.00	+0.39	+1.39
1-hexene	−1.37	+3.74	−1.03	+0.87	−0.00	+0.65
1-heptene	−2.43	+0.24	−2.12	+0.41	−1.37	−0.65
1-octene	−3.21	−1.08	−2.95	−0.34	−2.77	−1.72
1-decene	−1.53	−1.17	+0.45	−2.80	−1.30	−0.32
1-dodecene	−6.32	−4.40	−2.54	−5.65	−2.02	−1.04
1-tridecene	+2.14	−1.62	+2.37	−0.17	−2.66	+3.47
1-tetradecene	+4.47	−0.94	+4.65	+0.63	−1.70	+6.04
1-pentadecene	+1.75	−5.13	+1.95	−3.96	−5.45	+3.57
1-hexadecene	+6.69	−2.16	+6.83	−1.51	−2.16	+8.99
1-octadecene	+3.00	−8.77	+3.15	−9.62	−7.85	+6.23
1-eicosene	+7.11	−8.51	+7.19	−10.61	−6.49	+11.84

TABLE 3. Unbranched alkanes. Absolute percent error for tested methods for different chain length

Chain length	Ambrose	Joback	Somayajulu	Daubert	Constantinou	Marrero–Gani
C_2–C_{10}	0.41	2.42	0.54	2.23	3.43	2.98
C_{11}–C_{20}	4.12	5.28	4.29	4.99	3.70	6.31
C_{21}–C_{28}	15.13	9.21	15.13	17.4	3.14	25.2

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TABLE 4. Branched alkanes. The dependence of absolute percent errors of the tested methods upon the number of C atoms in a molecule

Number of C atoms	Ambrose	Joback	Somayajulu	Daubert	Constantinou	Marrero–Gani
4	3.78	7.84	0.16	2.25	8.49	8.38
5	4.64	7.28	0.97	2.76	7.42	6.62
6	0.25	1.66	1.04	0.97	1.84	1.09
7	0.52	2.50	1.57	1.10	2.10	2.18
8	0.47	3.22	1.16	1.42	2.19	2.03
9	1.06	6.21	1.30	2.09	3.92	6.78
10–16	0.63	8.00	2.03	4.33	5.26	7.34

surement was a principal objective of the experiment, as well as to know the purity of the substance sample used. Moreover the measurement error has been allocated for each experimental value collected in data banks.[13,14]

That information allowed us to form verified "subsets" concerning one property for one substance and containing reliable experimental data extracted from data banks mentioned. Any outliers were eliminated from every subset. The accepted data were then examined for their precision and accuracy as stated by the author. For individual cases of single or double data the selection of the reliable P_c values was additionally guided by auxiliary information, such as citation in the newest literature or comparison with data from auxiliary sources.[29] In these instances, the recommended values, denoted with asterisks, are those from a single investigation and occur only in Table 1. Secondary data, values that were not derived from the original observation on P_c, have been rejected.

The same selection has been performed for T_b for 12 substances not mentioned in Part I.[1] For those substances, denoted with letter "a" in Table 1, the recommended data set has been created in this study. The rest of 275 (for substances used for testing and calculating purpose) needed T_b values were taken from Part I.[1]

3.1.1. Statistical Analysis of Selected Data

The reliable values of T_b and P_c were selected as the closest to the weighted mean of all measured data included in individual subsets. It was feasible because each experimental value had its measurement error used subsequently for determination of weights of experimental values. A more detailed description of applied statistical selection is included in Part I.[1]

3.2. Recommended Experimental Data on Critical Pressures for Aliphatic Hydrocarbons

Data banks[13,14] include about 7–10 data values for P_c per substances up to C_9 and about 2–3 data values for C_9-C_{20} substances allocated in Table 1. Critical analysis of the data mentioned reduced those numbers to: 4–6 and 2–3, respectively. The experimental T_b[1] and P_c[13,14] values of 95 aliphatic hydrocarbons, mentioned in point 1(a), were used for evaluation of the critical pressure prediction methods. Names of those substances together with recommended experimental data on T_b and P_c are listed in Table 1.

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4. Testing Calculations

The testing calculations, performed for evaluation of accuracy of six predictive methods, were conducted for 95 hydrocarbons including branched and unbranched: alkanes, alkenes, and alkynes.

The chosen prediction methods employ from 20 to 200 specific contribution groups together with attributed pressure correction factors Δp_i. For each hydrocarbon and for each method all contribution groups forming the molecule were specified and their sum $(\Sigma n_i \Delta p_i)$ yield values of final correction factor used for prediction of critical pressure P_{cp}.

Most of tested methods require the knowledge of:

(1) group contribution models based on molecular structure, and

TABLE 5. Branched alkanes. The dependence of absolute percent errors of tested methods upon the number of substituted CH_3–groups to main chain

Number of Substituted CH_3 groups	Ambrose	Joback	Somayajulu	Daubert	Constantinou	Merreo–Gani
1	0.73	2.18	1.26	1.32	2.03	1.90
2	1.10	2.97	1.35	1.27	2.44	2.18
3	0.70	4.62	1.71	1.21	3.87	3.07
4	1.95	8.31	1.88	2.78	4.16	10.01

TABLE 6. The dependence of absolute percent errors of tested methods upon the C_s/C_m ratio

C_s/C_m ratio	Ambrose	Joback	Somayajulu	Daubert	Constantinou	Marrero–Gani
0.12–0.16	0.455	1.11	0.69	1.30	0.78	0.81
0.20–0.33	0.74	2.73	0.93	1.15	2.42	2.20
0.40–0.50	0.43	3.03	1.56	1.29	2.59	2.40
0.60–0.75	1.39	1.30	1.49	2.16	4.27	5.66
0.77–0.80	1.16	9.70	2.01	3.92	7.08	8.52

(2) molecular weight.

The method of Daubert[6,7] required additionally the knowledge of T_b and T_c values. T_c value is being automatically determined during the calculation process of P_c, as an auxiliary parameter. This auxiliary parameter may be experimentally determined and then used for calculation. It is obvious that the calculated T_c value is less accurate than a measured one, but for the purpose of testing, the experimental T_c values were not used since only one critical parameter was measured for a substance. That is why there is a rare need to employ any T_c value for P_c prediction, since experimental data on both of them or none of them are mostly available.

Deviations of calculated critical temperatures P_{cp} from recommended experimental values of P_c are shown in Table 2. They were calculated according to:

$$E=[(P_{cp}-P_c)/P_c]\cdot 100$$

where P_c=experimental recommended value of critical pressure; and P_{cp}=value of critical pressure obtained from prediction method.

Error E values are listed with accuracy of 0.01%.

5. Results of Tests

5.1. Alkanes

The method of Joback[4] is not recommended for molecules consisting of CH_2–substituant, since the correction factor for that group equals zero. It leads to significant errors, particularly for substances having long chains, built of $-CH_2-$ groups. This fact is reflected in the results of testing for branched as well as for unbranched alkanes.

5.1.1. Unbranched Alkanes

Deviations of calculated P_c from experimental values for the hydrocarbons (C_1-C_{28}) (Tables 2 and 3) increase with the chain length. In the range C_1-C_{10} the Ambrose[3] and Somayajulu[5] methods give deviations below 0.5%. Constantinou[8] and Ambrose[3] yield less deviations below 4% in the region of $C_{11}-C_{20}$. The sudden increase of the error is observed for $C_{21}-C_{28}$ hydrocarbons (Table 3). In this range only the Constantinou[8] method gives the lowest error of about 3.2% and this method is recommended for high molecular weight aliphatic unbranched hydrocarbons.

5.1.2. Branched Alkanes

The investigation was performed for branched alkanes with methyl substituants, since experimental data on P_c are mainly available for this group. No reliable experimental data for other aliphatic substituants have been found. The influence of the chain length as well as of the number of CH_3– groups on the method's errors were examined. All results of the investigation are presented in Tables 4–6.

Most of the methods—except Somayajulu[5]—yield significantly large deviations in the C_2-C_5 range (Table 4). This maximum may be related to an influence of relatively large substituants on a small molecule. The fluctuation of error value due to the length of the main chain allows one to distinguish the method of Ambrose[3] yielding the lowest errors.

The dependence of error on the number of substituted CH_3– groups was investigated too. The results are presented in Table 5. The considerable increase in error was observed in the case of four substituted CH_3– groups. Ambrose,[3] Daubert,[6,7] and Somayajulu[5] seem to be more accurate than others.

In Table 6 the deviation values due to the C_s/C_m ratio are presented, where C_m is the number of C atoms in a main chain and C_s is the number of all C atoms in side chains. The C_s/C_m ratio reflects the branching extent of molecules, which has a significant influence on the accuracy of selected methods. The results are presented in Table 6. The accuracy of the Joback[4] and Marrero[9,10] methods are strongly sensitive to the C_s/C_m ratio, while the Somayajulu[5] and Ambrose[3] methods deviations do not depend on the ratio mentioned and yield a constant error level like: 0.7%–2.0% for Somayajulu[5] and 0.5%–1.2% for Ambrose.[3]

Thus these two methods are mainly recommended for calculation of critical pressures for branched alkanes. Both of them take the branching into consideration, employing Platt number[3] and gauche position.[5] In this work the methods mentioned were employed for calculation of missing values of critical pressures of branched alkanes.

5.2. Alkenes, Alkynes

The results of testing (Table 2) proved that no particular method may be generally recommended for all alkenes and

TABLE 7. Alkenes, alkynes, Absolute percent errors for tested methods

Ambrose	Joback	Somayajulu	Daubert	Constantinou	Marrero–Gani
3.27	3.14	2.33	2.50	2.87	3.70

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TABLE 8. Branched alkanes. Calculated values of critical pressures (P_{cp}) obtained by the Ambrose[3] method. Expected absolute percent error for all P_{cp}-less than 3.3%. Values of critical pressure using Somayajulu[5] method-P_{cp1} are given in the second column for comparison purpose. T_b^1=experimental normal boiling temperatures, used for calculation critical pressures

CAS RN	Formula	Name	P_{cp} (kPa) Ambrose	P_{cp1} (kPa) Somayajulu	T_b (K)
3074-71-3	C_9H_{20}	2,3-dimethylheptane	2406	2386	413.15
2213-23-2	C_9H_{20}	2,4-dimethylheptane	2352	2386	405.65
2216-30-0	C_9H_{20}	2,5-dimethylheptane	2352	2386	407.65
1072-05-5	C_9H_{20}	2-6-dimethylheptane	2301	2325	408.35
4032-86-4	C_9H_{20}	3,3-dimethylheptane	2444	2475	410.16
922-28-1	C_9H_{20}	3,4-dimethylheptane	2461	2449	413.85
926-82-8	C_9H_{20}	3,5-dimethylheptane	2406	2449	408.65
1067-20-5	C_9H_{20}	3,3-diethylpentane	2558	2611	419.32
1068-19-5	C_9H_{20}	4,4-dimethylheptane	2444	2475	407.50
16747-33-4	C_9H_{20}	3-ethyl-2,3-dimethylpentane	2513	2640	414.75
16747-25-4	C_9H_{20}	2,2,3-trimethylhexane	2513	2502	407.40
16747-26-5	C_9H_{20}	2,2,4-trimethylhexane	2456	2437	399.69
16747-28-7	C_9H_{20}	2,3,3-trimethylhexane	2572	2570	409.45
921-47-1	C_9H_{20}	2,3,4-trimethylhexane	2531	2475	412.21
1069-53-0	C_9H_{20}	2,3,5-trimethylhexane	2418	2411	404.52
16747-30-1	C_9H_{20}	2,4,4-trimethylhexane	2456	2502	403.60
16747-31-2	C_9H_{20}	3,3,4-trimethylhexane	2513	2570	413.57
16789-46-1	C_9H_{20}	3-ethyl-2-methylhexane	2406	2449	411.15
3074-76-8	C_9H_{20}	3-ethyl-3-methylhexane	2500	2542	413.75
3074-77-9	C_9H_{20}	3-ethyl-4-methylhexane	2461	2515	413.55
3074-75-7	C_9H_{20}	4-ethyl-2-methylhexane	2406	2449	406.95
15869-80-4	C_9H_{20}	3-ethylheptane	2393	2423	416.25
2216-32-2	C_9H_{20}	4-ethylheptane	2393	2423	414.35
2216-33-3	C_9H_{20}	3-methyloctane	2340	2361	417.35
2216-34-4	C_9H_{20}	4-methyloctane	2340	2361	415.58
16747-32-3	C_9H_{20}	3-ethyl-2,2-dimethylpentane	2513	2570	406.96
1068-87-7	C_9H_{20}	2,4-dimethyl-3-ethylpentane	2531	2475	409.81
7146-60-3	$C_{10}H_{22}$	2,3-dimethyloctane	2214	2198	437.80
15869-89-3	$C_{10}H_{22}$	2,5-dimethyloctane	2169	2198	430.15
1072-16-8	$C_{10}H_{22}$	2,7-dimethyloctane	2126	2147	433.15
4110-44-5	$C_{10}H_{22}$	3,3-dimethyloctane	2246	2272	434.35
15869-93-9	$C_{10}H_{22}$	3,5-dimethyloctane	2169	2198	432.65
14720-74-2	$C_{10}H_{22}$	2,2,4-trimethylheptane	2211	2240	422.55
1190-83-6	$C_{10}H_{22}$	2,2,6-trimethylheptane	2166	2188	421.15
2613-61-8	$C_{10}H_{22}$	2,4,6-trimethylheptane	2180	2219	419.00
1189-99-7	$C_{10}H_{22}$	2,5,5-trimethylheptane	2257	2295	425.95
4032-94-4	$C_{10}H_{22}$	2,4-dimethyloctane	2169	2198	429.05
2051-30-1	$C_{10}H_{22}$	2,6-dimethyloctane	2169	2198	431.65
871-83-0	$C_{10}H_{22}$	2-methylnonane	2116	2126	440.15
17302-02-2	$C_{10}H_{22}$	3-ethyl-3-methylheptane	2293	2328	437.05
5911-04-6	$C_{10}H_{22}$	3-methylnonane	2159	2177	440.65
15869-85-9	$C_{10}H_{22}$	5-methylnonane	2159	2177	438.25
52987-09-3	$C_{10}H_{22}$	2,2,3,5-tetramethylhexane	2315	2317	422.15
52897-10-6	$C_{10}H_{22}$	2,3,3,4-tetramethylhexane	2522	2496	437.74
52897-11-7	$C_{10}H_{22}$	2,3,3,5-tetramethylhexane	2365	2375	426.15
52897-12-8	$C_{10}H_{22}$	2,3,4,4-tetramethylhexane	2468	2434	434.75
52897-15-1	$C_{10}H_{22}$	2,3,4,5-tetramethylhexane	2330	2295	429.15
5171-84-6	$C_{10}H_{22}$	3,3,4,4-tetramethylhexane	2619	2586	443.15
52896-99-8	$C_{10}H_{22}$	4-ethyl-2,2-dimethylhexane	2257	2295	420.15
17301-94-4	$C_{10}H_{22}$	4-methylnonane	2159	2177	441.15
15869-96-2	$C_{10}H_{22}$	4,5-dimethyloctane	2260	2250	436.15
16747-44-7	$C_{10}H_{22}$	2,2,3,3,4-pentamethylpentane	2574	2548	439.20
52897-18-4	$C_{10}H_{22}$	3-ethyl-2,2,4-trimethylpentane	2416	2375	428.45
52897-19-5	$C_{10}H_{22}$	3-ethyl-2,3,4-trimethylpentane	2522	2496	442.59

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TABLE 8. Branched alkanes. Calculated values of critical pressures (P_{cp}) obtained by the Ambrose[3] method. Expected absolute percent error for all P_{cp}-less than 3.3%. Values of critical pressure using Somayajulu[5] method-P_{cp1} are given in the second column for comparison purpose. T_b^1=experimental normal boiling temperatures, used for calculation critical pressures—Continued

CAS RN	Formula	Name	P_{cp} (kPa) Ambrose	P_{cp1} (kPa) Somayajulu	T_b (K)
16747-45-8	$C_{10}H_{22}$	2,2,3,4,4-pentamethylpentane	2464	2423	432.44
13475-79-1	$C_{10}H_{22}$	2,4-dimethyl-3-isopropylpentane	2330	2295	430.19
6975-98-0	$C_{11}H_{24}$	2-methyldecane	1967	1976	462.27
2847-72-5	$C_{11}H_{24}$	4-methyldecane	2004	2019	461.25
61868-46-0	$C_{11}H_{24}$	2,2,4,6-tetramethylheptane	2056	2091	435.05
61198-87-2	$C_{12}H_{26}$	2,2,3,5,6-pentamethylheptane	2064	1960	461.95
13475-82-6	$C_{12}H_{26}$	2,2,4,6,6-pentamethylheptane	1945	1977	450.95
92867-09-9	$C_{15}H_{32}$	6-propyldodecane	1599	1615	524.75
2801-86-7	$C_{16}H_{34}$	7,8-dimethyltetradecane	1516	1512	543.15
2882-96-4	$C_{16}H_{34}$	3-methylpentadecane	1471	1479	539.45
500014-84-6	$C_{20}H_{42}$	3-ethyloctadecane	1226	1233	614.15
630-01-3	$C_{26}H_{54}$	hexacosane	949	949	534.15

alkynes of the range C_2-C_{20} due to significant fluctuation of errors for individual methods and types of compounds. The average deviations are contained in the range 0.04%–11%. No regularity in accuracy due the molecular structure has been observed. That is why every case (that is substance) must be treated individually. For the whole group the authors recommend the methods of Somayajulu,[5] Daubert,[6,7] and Constantinou,[8] based on the general results presented in Table 7.

When choosing the method for individual substance one should take into consideration that: the Constantinou[8] method yields significant accuracy (higher than that of Somayajulu[5] and Daubert[6,7]) only in cases of hydrocarbons represented in the second-order group contribution; two methods provide corrections for *cis*- (Daubert[6,7]) and *trans*-(Somayajulu[5]) types of bond; and those methods should be preferred in *cis/trans* cases.

6. Prediction of Critical Pressures

Based on the conclusions from the analysis of the results of examination (Secs. 4 and 5) the proper prediction methods have been applied for calculation of critical pressures for aliphatic hydrocarbons. The Ambrose[3] and Somayajulu[5] methods were chosen for branched alkanes as the most accurate and not sensitive to branching, which is the most universal. The calculated values of P_c are listed in Table 8.

Unlike alkanes, no particular method could be applied for all alkenes. In every case, each substance was considered separately (that is the particular method and particular hydrocarbon). Somayajulu,[5] Daubert,[6,7] and Constantinou[8] methods were used in every individual case due to the conclusions in point 5.2. The calculated values of critical pressures, P_{cp}, of alkenes, alkynes are listed in Table 9. The expected percent errors, noted in the headers of Tables 8 and 9, result from the analysis of the accuracy of applied predictive methods.

7. Conclusions and Recommendations

The main result of this work is the set of critical pressures for 180 aliphatic hydrocarbons for which experimental critical data were not available in the literature (Tables 8 and 9).

The other results of this work are the sets of:

(1) Recommended experimental data on critical pressures of 95 aliphatic hydrocarbons, used for testing purposes (Table 1). Some of presented values, denoted by asterisks, are derived from a reliable source, but from a single investigation (Table 1). Despite this they tally with other literature but not experimental data; their reliability may be lower than that of the rest presented P_c values.

(2) Recommended experimental data on normal boiling points of 12 aliphatic hydrocarbons (Tables 1 and 9).

A further result is determination of the accuracy of particular prediction methods for specific subgroups of aliphatic hydrocarbons. The analyses of every tested method were performed in 2004 based on the experimental databases (NIST-TRC)[13] and (TDC).[14] The latter one is being permanently updated up to 2005.

The methods of Ambrose[3] and Somayajulu[5] are recommended for branched alkanes. Mentioned methods yield the lesser deviations (Tables 4 and 5) which are not sensitive to branching ratio (Table 6). Though no particular method is recommended for alkenes and alkynes, the authors suggest employing three methods, giving satisfactory results as shown in Tables 2 and 7: Somayajulu,[5] Daubert,[6,7] and Constantinou.[8] More detailed guidelines regarding application of the mentioned methods are presented in Secs. 5.1 and 5.2.

Predictive methods still remain an important source of obtaining critical data as the world literature experimental critical data resources are really poor. The number of substances for which any critical property is measured is relatively low,

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TABLE 9. Alkenes and alkynes. Calculated values of critical pressures (P_{cp}) predicted using one of the selected methods, specified below. Expected percent error for all (P_{cp})-(from 1.18% to 3.31%). T_b^l=experimental normal boiling point temperature. E=expected percent errors for individual cases. Numbers attributed to methods: (1) Somayajulu,[5] (2) Daubert,[7] (3) Constantinou[8]

CAS RN	Formula	Name	P_{cp} (KPa)	E (%)	Method	T_b (K)
503-17-3	C_4H_6	2-butyne	5049	2.33	1	300.12
598-25-4	C_5H_8	3-methyl-1,2-butadiene	3965	2.33	1	313.95
591-96-8	C_5H_8	2,3-pentadiene	4105	2.33	1	321.35
646-04-8	C_5H_{10}	*trans*-2-pentene	3515	2.33	1	309.50
2206-23-7	C_5H_6	3-penten-1-yne	4556	2.33	1	317.05
628-16-0	C_6H_6	1,5-hexadiyne	4305	2.33	1	359.15
592-42-7	C_6H_{10}	1,5-hexadiene	3378	2.33	1	332.55
922-59-8	C_6H_{10}	3-methyl-1-pentyne	3609	2.33	1	330.85
7154-75-8	C_6H_{10}	4-methyl-1-pentyne	3469	2.33	1	334.45
764-35-2	C_6H_{10}	2-hexyne	3715	2.33	1	357.67
21020-27-9	C_6H_{10}	4-methyl-2-pentyne	3627	2.33	1	346.28
513-81-5	C_6H_{10}	2,3-dimethyl-1,3-butadiene	3409	2.50	2	343.15
760-20-3	C_6H_{12}	3-methyl-1-pentene	3227	2.33	1	327.37
928-49-4	C_6H_{10}	3-hexyne	3715	2.33	1	354.45
616-12-6	C_6H_{12}	*trans*-3-methyl-2-pentene	3253	2.33	1	343.50
674-76-0	C_6H_{12}	*trans*-4-methyl-2-pentene	3068	2.33	1	331.70
563-78-0	C_6H_{12}	2,3-dimethyl-1-butene	3227	2.33	1	328.76
760-21-4	C_6H_{12}	2-ethyl-1-butene	3217	2.50	2	340.65
763-29-1	C_6H_{12}	2-methyl-1-pentene	3299	2.33	1	335.26
616-12-6	C_6H_{12}	*trans*-3-methyl-2-pentene	3253	2.33	1	343.50
674-76-0	C_6H_{12}	*trans*-4-methyl-2-pentene	3068	2.33	1	331.70
558-37-2	C_6H_{12}	3,3-dimethyl-1-butene	3230	2.50	2	314.43
7688-21-3	C_6H_{12}	*cis*-2-hexane	3308	2.50	2	342.01
7642-09-3	C_6H_{12}	*cis*-3-hexene	3271	2.50	2	339.65
922-62-3	C_6H_{12}	*cis*-3-methyl-2-pentene	3205	2.50	2	340.86
691-38-3	C_6H_{12}	*cis*-4-methyl-2-pentene	3241	2.50	2	329.45
4050-45-7	C_6H_{12}	*trans*-2-hexene	3135	2.33	1	340.24
922-61-2	C_6H_{12}	3-methyl-2-pentene	3132	2.87	3	340.65
594-56-9	C_7H_{14}	2,3,3-trimethyl-1-butene	2975	2.33	1	350.85
13269-52-8	C_6H_{12}	*trans*-3-hexene	3135	2.33	1	340.30
2203-80-7	C_7H_{12}	5-methyl-1-hexyne	3167	2.50	2	364.65
21020-26-8	C_7H_{12}	3-ethyl-1-pentyne	3196	2.33	1	360.15
13361-63-2	C_7H_{12}	4,4-dimethyl-1-pentyne	3288	2.33	1	349.23
1000-86-8	C_7H_{12}	2,4-dimetyl-1,3-pentadiene	2932	2.50	2	366.90
20198-49-6	C_7H_{12}	4-methyl-2-hexyne	3324	2.33	1	372.69
53566-37-3	C_7H_{12}	5-methyl-2-hexyne	3324	2.33	1	375.61
4049-81-4	C_7H_{12}	2-methyl-1,5-hexadiene	3121	2.33	1	362.00
999-78-0	C_7H_{12}	4,4-dimethyl-2-pentyne	3189	2.33	1	356.15
2586-89-2	C_7H_{12}	3-heptyne	3277	2.33	1	380.31
36566-80-0	C_7H_{12}	2-methyl-3-hexyne	3210	2.33	1	368.35
2384-90-9	C_7H_{12}	1,2-heptadiene	3017	2.33	1	376.90
1541-23-7	C_7H_{12}	1,5-heptadiene	3095	2.33	1	366.85
3404-72-6	C_7H_{14}	2,3-dimethyl-1-pentene	2994	2.33	1	357.50
10574-37-5	C_7H_{14}	2,3-dimethyl-2-pentene	3029	2.33	1	370.55
2213-32-3	C_7H_{14}	2,4-dimethyl-1-pentene	2994	2.33	1	354.73
6094-02-6	C_7H_{14}	2-methyl-1-hexane	2954	2.33	1	364.65
692-24-0	C_7H_{14}	*trans*-2-methyl-3-hexene	2771	2.33	1	359.02
3899-36-3	C_7H_{14}	*trans*-3-methyl-3-hexene	2918	2.33	1	366.67
3404-71-5	C_7H_{14}	2-ethyl-1-pentene	2954	2.33	1	365.55
7357-93-9	C_7H_{14}	2-ethyl-3-methyl-1-butene	2994	2.33	1	362.05
3404-73-7	C_7H_{14}	3,3-dimethyl-1-pentene	2975	2.33	1	350.69
7385-78-6	C_7H_{14}	3,4-dimethyl-1-pentene	3054	2.33	1	353.93
4038-04-4	C_7H_{14}	3-ethyl-1-pentene	2994	2.33	1	357.28
3404-61-3	C_7H_{14}	3-methyl-1-hexene	2897	2.33	1	357.09
762-62-9	C_7H_{14}	4,4-dimethyl-1-pentene	2975	2.33	1	345.35
3769-23-1	C_7H_{14}	4-methyl-1-hexene	2994	2.33	1	359.97
3524-73-0	C_7H_{14}	5-methyl-1-hexene	2897	2.33	1	358.65

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TABLE 9. Alkenes and alkynes. Calculated values of critical pressures (P_{cp}) predicted using one of the selected methods, specified below. Expected percent error for all (P_{cp})-(from 1.18% to 3.31%). T_b^l=experimental normal boiling point temperature. E=expected percent errors for individual cases. Numbers attributed to methods: (1) Somayajulu,[5] (2) Daubert,[7] (3) Constantinou[8]—Continued

CAS RN	Formula	Name	P_{cp} (KPa)	E (%)	Method	T_b (K)
6443-92-1	C_7H_{14}	*cis*-2-heptene	2946	2.50	2	371.56
15840-60-5	C_7H_{14}	*cis*-2-methyl-3-hexene	2861	2.50	2	359.80
7642-10-6	C_7H_{14}	*cis*-3-heptene	2873	2.50	2	368.90
10574-36-4	C_7H_{14}	*cis*-3-methyl-2-hexene	2863	2.50	2	370.41
4914-89-0	C_7H_{14}	*cis*-3-methyl-3-hexene	2875	2.50	2	368.47
690-08-4	C_7H_{14}	*trans*-4,4-dimethyl-2-pentene	2951	2.87	3	349.89
762-63-0	C_7H_{14}	*cis*-4,4-dimethyl-2-pentene	3021	2.50	2	353.15
14686-13-6	C_7H_{14}	*trans*-2-heptene	2824	2.33	1	371.06
3683-19-0	C_7H_{14}	*cis*-4-methyl-2-hexene	2931	2.50	2	359.50
4914-92-5	C_7H_{14}	*trans*-3,4-dimethyl-2-pentene	2862	2.33	1	364.75
14686-14-7	C_7H_{14}	*trans*-3-heptene	2824	2.33	1	368.81
20710-38-7	C_7H_{14}	*trans*-3-methyl-2-hexene	2918	2.33	1	368.38
3683-22-5	C_7H_{14}	*trans*-4-methyl-2-hexene	2862	2.33	1	360.79
7385-82-2	C_7H_{14}	*trans*-5-methyl-2-hexene	2862	2.33	1	361.27
2738-19-4	C_7H_{14}	2-methyl-2-hexene	2829	2.50	2	368.25
15870-10-7	C_8H_{16}	2-methyl-1-heptene	2672	2.33	1	392.37
2809-67-8	C_8H_{14}	2-octyne	2931	2.33	1	411.24
764-13-6	C_8H_{14}	2,5-dimethyl-2,4-hexadiene	2850	2.33	1	407.65
627-58-7	C_8H_{14}	2,5-dimethyl-1,5-hexadiene	2894	2.33	1	387.45
32388-99-1	C_8H_{14}	*trans*-2-ethyl-3-methyl-1,3-pentadiene	2693	2.33	1	381.15
32388-90-2	C_8H_{14}	*cis*-2-ethyl-3-methyl-1,3-pentadiene	2712	2.50	2	400.15
14850-22-7	C_8H_{16}	*cis*-3-octene	2676	2.50	2	396.04
14919-01-8	C_8H_{16}	*trans*-3-octene	2568	2.33	1	396.44
4810-09-7	C_8H_{16}	3-methyl-1-heptene	2626	2.33	1	384.15
13151-05-8	C_8H_{16}	4-methyl-1-heptene	2705	2.33	1	385.65
5026-76-6	C_8H_{16}	6-methyl-1-heptene	2632	2.50	2	386.35
16746-86-4	C_8H_{16}	2,3-dimethyl-1-hexene	2705	2.33	1	383.69
7145-20-2	C_8H_{16}	2,3-dimethyl-2-hexene	2732	2.33	1	395.00
627-97-4	C_8H_{16}	2-methyl-2-heptene	2540	2.87	3	395.77
13151-04-7	C_8H_{16}	5-methyl-1-heptene	2626	2.33	1	386.15
1632-16-2	C_8H_{16}	2-ethyl-1-hexene	2753	2.33	1	391.85
39761-64-3	C_8H_{16}	3,4,4-trimethyl-*cis*-2-pentene	2735	2.50	2	385.45
560-23-6	C_8H_{16}	2,3,3-trimethyl-1-pentene	2771	2.33	1	381.46
690-92-6	C_8H_{16}	2,2-dimehyl-*cis*-3-hexene	2683	2.50	2	378.95
3404-80-6	C_8H_{16}	2-ethyl-4-methyl-1-pentene	2786	2.33	1	380.65
692-96-6	C_8H_{16}	*trans*-2-methyl-3-heptene	2524	2.33	1	387.13
7300-03-0	C_8H_{16}	3-methyl-3-heptene	2504	2.50	2	394.35
690-93-7	C_8H_{16}	*trans*-2,2-dimethyl-3-hexene	2511	2.33	1	374.05
61847-78-7	C_8H_{16}	*trans*-2,4-dimethyl-3-hexene	2524	2.33	1	380.75
37549-89-6	C_8H_{16}	*cis*-2,4-dimethyl-3-hexene	2490	2.50	2	382.15
3404-75-9	C_8H_{16}	3-methyl-2-heptene	2540	2.87	3	394.65
19550-88-0	C_8H_{16}	*trans*-3,4-dimethyl-3-hexene	2388	2.33	1	387.95
7116-86-1	C_8H_{16}	5,5-dimethyl-1-hexene	2690	2.33	1	376.25
500007-01-2	C_8H_{16}	5-methyl-1-heptene	2705	2.33	1	386.65
500015-77-0	C_9H_{16}	2,3,3,4-tetramethyl-1,4-pentadiene	2565	2.33	1	400.85
4588-18-5	C_9H_{18}	2-methyl-1-octene	2439	2.33	1	418.00
20442-63-1	C_9H_{18}	2,3,3,4-tetramethyl-1-pentene	2547	2.33	1	406.35
500001-23-0	C_9H_{18}	2,4-dimethyl-3-ethyl-2-pentene	2515	2.33	1	403.12
53907-59-8	C_9H_{18}	3-ethyl-4,4-dimethyl-2-pentene	2503	2.33	1	407.18
2384-85-2	$C_{10}H_{18}$	3-decyne	2418	2.33	1	448.65
19398-37-9	$C_{10}H_{20}$	*cis*-3-decene	2247	2.50	2	446.4
2129-95-5	$C_{10}H_{20}$	2-methyl-2-nonene	2113	2.87	3	444.15
53966-53-3	$C_{10}H_{20}$	2-methyl-3-nonene	2121	2.87	3	434.15
39083-38-0	$C_{10}H_{20}$	3,4,5,5-tetramethyl-2-hexene	2318	2.33	1	425.15
5857-68-1	$C_{10}H_{20}$	2,2,4,4-tetramethyl-3-methylene	2322	2.33	1	423.45
500006-47-3	$C_{10}H_{20}$	3-ethyl-2,4,4-trimethyl-2-pentene	2295	2.33	1	419.75

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currently just over 400 (including about 180 hydrocarbons as a whole group). Many of these values are quite old, and the accuracy of some of these older values is questionable. The lacks will be complemented by means of the best and most updated methods. This study will be followed by the next one, dealing with critical pressure of aromatic and cyclic hydrocarbons. Further studies will be concerned with critical parameters of oxygen and halogen derivatives of hydrocarbons, as well as with evaluation and employing new predictive methods.

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