New correlations for predicting thermodynamic properties of hydrocarbons in the ideal gas state

Abstract

A new empirical correlation is developed for the accurate prediction of isobaric heat capacity, enthalpy, and entropy of pure hydrocarbons and petroleum fractions in the ideal gas state, with a particular emphasis on the low-temperature region (200–300 K). Unlike traditional models such as Kesler-Lee, Huang, and Kuznetsov, which are often limited in accuracy or applicability at low temperatures or for heavy hydrocarbons, the proposed correlation integrates a fourth-degree polynomial approach and molecular weight dependence to extend predictive capabilities across a broad range of components—from butane to heavy fractions exceeding 570 g/mol. Validation against 340 experimental data points for heat capacity and 112 data points for enthalpy and entropy shows a significant reduction in AARE and MARE values, achieving errors as low as 0.90% and 2.10%, respectively. While the correlation provides excellent results for normal alkanes, its applicability to cycloalkanes and aromatic hydrocarbons is limited and may require further refinement. The proposed model holds strong potential for implementation in thermodynamic simulators for oil, gas, and condensate production and processing, especially under surface conditions where precise thermophysical data at subambient temperatures are critical.

Key words: heat capacity, enthalpy, entropy, ideal gas state, thermodynamic correlation, petroleum fractions

Introduction

The integration of new technologies in oil and gas industry imposes increasing demands on engineers' knowledge, particularly in understanding the behavior of complex systems. For efficient design of chemical, petrochemical, and biochemical processes in a wide range of pressures and temperatures, accurate data on the thermodynamic properties of pure hydrocarbons and petroleum fractions are required. Phase behavior and thermal properties needed for design of technological processes are typically not determined for all compounds and must be estimated using thermodynamic models.

In petroleum engineering models based on equations of state are widely used for thermodynamic properties calculation as they allow to predict phase state and thermodynamic properties under a wide range of pressure and temperature. Most of these models use ideal gas state as a reference state for thermodynamic calculations. Thus, for accurate simulations of technological processes, it is necessary to know the properties of fluid inthe ideal gas state over a wide range of thermobaric conditions. According to thermodynamic relations, most functions of the ideal gas state can be derived from the heat capacity.

One of the earliest correlations for the ideal gas heat capacity for hydrocarbons was proposed in [1,2] and wasdescribed by a polynomial function of temperature. Aly and Lee [3] introduced expressions for the ideal gas heat capacity derived theoretically from thermodynamic relations. This method provides accurate predictions of heat capacity, enthalpy and entropy for many compounds over a temperature range from 300 K to 1500 K. Coniglio et al. [4] developed approaches based on statistical mechanics that allow the calculation of the ideal gas heat capacity below 300 K. However, authors considered only a limited number of compounds, and their approaches cannot be applied to complex mixtures such as crude oil.

Correlations for thermodynamic properties of various gases in the ideal gas state, based on the molecular structure of fluid compounds, can be found in [5-8]. However, due to the discrete nature of the data set, there are some definite limitations to the use of the correlations they propose.

Heavy hydrocarbons have a large number of isomers, which requires an increased number of initial parameters for accurate heat capacity estimation. Attempts have been made to use critical parameters (pressure, temperature, volume), Watson characterization factor, acentric factor, molecular weight, and other parameters to calculate thermodynamic properties. Each of the parameters can be independently estimated using the graphical methods of Watson and Nelson [9], API [10], and one of the analytical correlations of Cavett[11], Kesler-Lee [12], Lee-Kesler [13], Riazi-Daubert [14,15], Riazi-Sahhaf [16], Twu [17], Pedersen [18-21], and Korsten [22], which are presented in details in the Riazi monograph [23].

Currently, in petroleum engineering the Kesler-Lee correlation [12] is the most usedfor calculation of petroleum fractions heat capacity.It is implemented in modern software for PVT simulations such as PVTSim Nova by Calsep, Multiflash by KBC, and Aspen HYSYS.

The correlations described above provide high accuracy in most cases, however, with the advancement of high-precision chromatography and more accurate computational methods, further modifications remain relevant.A universal correlation for determining the ideal gas heat capacities of large and complex molecules is presented in [24]. In the work [25], authors propose correlation for calculating heat capacity and enthalpy in the ideal gas state. It demonstrates significantly improved accuracy compared to the Kesler-Lee method, thereby opening new possibilities for more precise thermodynamic modeling of hydrocarbon systems. Meanwhile, for pure hydrocarbons, Kuznetsov proposed a simple correlation for heat capacity calculation based solely on the carbon number [26-27]. Despite its simplicity, this model is only applicable within thetemperature range from 298.15 to 1500 K.

In this work, we propose a new correlation for calculating the heat capacity, enthalpy, and entropy of petroleum fractions, extending its applicability to low temperatures down to 200 K. The obtained results are compared with established models from other authors.

Mathematical model

Heat capacity

Numerous correlations have been developed for calculating the heat capacity c_p^{id} of hydrocarbons in the ideal gas state for various conditions and parameters. In this section we'll consider the most common ones.

Kesler&Lee, 1976

Kesler& Lee correlation [12] is“classical”for most PVT software. They proposed two different models for calculation of c_p^{id}. The first correlation is presented for fractions C_{7+}[23]:

$$c_p^{id} = 4.1868\,M_w[C_0 + C_1T + C_2T^2], \tag{1}$$
$$C_0 = -0.32646 + 0.02678\,K_W - C_{F0}(0.084773 - 0.080809\,SG),$$
$$C_1 = [-2.5006 + 2.182\,K_W - 0.06845\,K_W^2 + C_{F0}(3.9191 - 3.7487\,SG)] \times 10^{-4},$$
$$C_2 = [-4.9874 - C_{F0}(2.54823 - 2.28171\,SG)] \times 10^{-7},$$
$$C_{F0} = \left[100\left(\frac{12.8}{K_W} - 1\right)\left(\frac{10}{K_W} - 1\right)\right]^2,$$
$$K_W = \frac{T_b^{1/3}}{SG},$$

where SG is specific gravity, which is approximately equal to the liquid density, T_b is the normal boiling temperature in K; K_W - Watson characterization factor; $M_w$is molecular weight in g/mol; c_p^{id} – heat capacity in the ideal gas state in J/mol· K); T is temperature in K.

The second Kesler and Lee (Lee-Kesler2) [24] correlation for direct calculation of c_p^{id} of petroleum fractions in terms of the Watson factor and acentric factor:

$$c_p^{id} = Mw[A_0 + A_1T + A_2T^2 - C_F(B_0 + B_1T + B_2T^2)], \tag{2}$$
$$A_0 = -1.41779 + 0.11828K_W,$$
$$A_1 = -(6.99724 - 8.69326K_W + 0.27715K_W^2) \times 10^{-4},$$
$$A_2 = -2.2582 \times 10^{-6},$$
$$B_0 = 1.09223 - 2.48245\omega,$$
$$B_1 = -(3.434 - 7.14\omega) \times 10^{-3},$$
$$B_2 = -(7.2661 - 9.2561\omega) \times 10^{-7},$$
$$C_F = \left[\frac{(12.8 - K_W)(10 - K_W)}{10\omega}\right]^2.$$

Acentric factor ω is defined from the following correlations [13].

For $T_{br} \le 0.8$

$$\omega = \frac{-ln\frac{P_c}{1.01325} - 5.92714 + \frac{6.09648}{T_{br}} + 1.28862ln(T_{br}) - 0.169347T_{br}^6}{15.2518 - \frac{15.6875}{T_{br}} - 13.4721\,ln(T_{br}) + 0.46577T_{br}^6}$$

For $T_{br} > 0.8$

$$\omega = -7.904 + 0.1352K_W - 0.007465K_W^2 + 8.359T_{br} + \frac{1.408 - 0.01063K_W}{T_{br}}$$

where $T_{br} = T_b/T_c$, P_c, T_c – critical pressure (bar) and temperature (K) of fraction respectively.

Huang, 2019

One more correlation is presented in [25]. Based on the experimental data for pure components from C_7 to C_{40} in the temperature range from 200 to1000 K the authors derived the following correlation using regression analysis:

$$c_p^{id} = M_w\begin{bmatrix} 0.0240296 + 0.0062421T - 2.60151 \times 10^{-6}T^2 + \\ +C_F(0.0022514 - 1.15054 \times 10^{-5}T + 2.39542 \times 10^{-8}T^2) \end{bmatrix}. \tag{3}$$

The designations and dimensions are the same as those presented earlier.

Kuznetsov, 2021

In 2021 Kuznetsov N.M. and Frolov S.M. proposed a simple analytical correlation for heat capacity and enthalpy [26]. They considered heat capacity and enthalpy of saturated hydrocarbons in the ideal gas state depending on temperature and on the number of carbon atoms in a molecule.

Using the experimental data for pure alkanes from C_5 to C_{20}, they derived the equation:

$$\begin{gathered} c_p^{id} = c_{p,5}(T) + g(T)(n-5), \\ c_{p,5}(T) = -4.0338 + 48.8733\tau - 2.5967\tau^2 + 0.0536\tau^3, \\ g(T) = -0.6528 + 9.3799\tau - 0.5309\tau^2 + 0.0116\tau^3, \end{gathered} \tag{4}$$

where τ is the dimensionless temperature in 100 K ($\tau = T/100$).

New correlation

As noted in [28], most correlations are derived for the temperature range from 300 K to 1500 K, and, therefore, cannot be reliably extrapolated to lower temperatures. Considering that the average boiling point of the C_{80} fraction is about 950 K [29], we will look for correlations in the range from 200 to 1000 K to calculate properties of fluid in the ideal gas state.

According to the experimental data from [25] given in Table 1, we'll plot the temperature dependence of c_p^{id} for n-alkanes C_7, C_{15}, C_{20}, C_{30}, and C_{40} (Figure 1).

Table 1 – Data used for fitting and testing isobaric heat capacity of petroleum fractions in the ideal gas state [25]

C_n	c_p^{id} (J/mol·K)									
	T (K)									
	200	298.15	300	400	500	600	700	800	900	1000
C_7	127.65	165.18	165.98	210.66	252.09	287.44	317.15	342.25	363.59	381.58
C_8	144.77	187.78	188.7	239.74	286.81	326.77	360.24	388.28	411.71	431.37
C_9	161.92	210.41	211.42	268.77	321.54	366.1	403.34	433.88	459.82	481.58
C_{10}	179.08	233.05	234.18	297.98	356.43	405.85	446.43	479.9	508.36	531.79
C_{11}	196.23	255.68	256.94	327.15	391.33	445.18	489.53	525.93	556.89	581.99
C_{12}	213.38	278.32	279.7	356.31	426.35	484.93	532.62	571.95	605.01	632.2
C_{13}	230.54	300.96	302.46	385.47	461.08	524.67	576.14	618.4	653.54	682.41
C_{14}	247.69	325.26	325.22	414.63	496.22	564	619.23	664.42	702.08	732.62
C_{15}	264.85	346.23	347.98	443.92	530.95	603.33	662.33	710.44	750.61	782.83
C_{16}	282	368.86	370.74	472.79	565.68	643.08	705.42	756.47	798.73	833.03
C_{17}	299.16	391.5	393.51	502.08	600.82	682.83	748.52	802.49	847.26	883.24
C_{18}	316.31	414.13	416.27	531.37	635.55	722.16	792.03	848.93	895.79	933.45
C_{19}	333.46	436.81	438.9	560.66	670.28	761.49	835.13	894.96	943.91	983.66
C_{20}	350.62	459.4	461.91	589.53	705.42	801.24	878.22	940.98	992.44	1033.87
C_{21}	367.77	482.04	484.67	618.69	740.32	840.77	921.4	987.09	1040.85	1084.07

C_{22}	384.93	504.67	507.44	647.85	775.21	880.31	964.58	1033.2	1089.26	1134.28
C_{23}	402.08	527.31	530.2	677.01	810.11	919.85	1007.76	1079.3	1137.67	1184.49
C_{24}	419.24	549.94	552.96	706.18	845	959.39	1050.94	1125.41	1186.08	1234.7
C_{25}	436.39	572.58	575.72	735.34	879.9	998.93	1094.12	1171.52	1234.49	1284.91
C_{26}	453.55	595.22	598.48	764.5	914.79	1038.47	1137.29	1217.63	1282.9	1335.11
C_{27}	470.7	617.85	621.24	793.66	949.68	1078.01	1180.47	1263.74	1331.31	1385.32
C_{28}	487.85	640.49	644	822.83	984.58	1117.55	1223.65	1309.84	1379.72	1435.53
C_{29}	505.01	663.12	666.76	851.99	1019.47	1157.09	1266.83	1355.95	1428.12	1485.74
C_{30}	522.16	685.76	689.52	881.15	1054.37	1196.62	1310.01	1402.06	1476.53	1535.95
C_{31}	539.32	708.39	712.28	910.31	1089.26	1236.16	1353.19	1448.17	1524.94	1586.15
C_{32}	556.47	731.03	735.05	939.48	1124.16	1275.7	1396.37	1494.27	1573.35	1636.36
C_{33}	573.63	753.66	757.81	968.64	1159.05	1315.24	1439.55	1540.38	1621.76	1686.57
C_{34}	590.78	776.3	780.57	997.8	1193.95	1354.78	1482.73	1586.49	1670.17	1736.78
C_{35}	607.94	798.93	803.33	1026.96	1228.84	1394.32	1525.9	1632.6	1718.58	1786.99
C_{36}	625.09	821.57	826.09	1056.13	1263.74	1433.86	1569.08	1678.7	1766.99	1837.19
C_{37}	642.24	844.21	848.85	1085.29	1298.63	1473.4	1612.26	1724.81	1815.4	1887.4
C_{38}	659.4	866.84	871.61	1114.45	1333.52	1512.93	1655.44	1770.92	1863.8	1937.61
C_{39}	676.55	889.48	894.37	1143.61	1368.42	1552.47	1698.62	1817.03	1912.21	1987.82
C_{40}	693.71	912.11	917.13	1172.78	1403.31	1592.01	1741.8	1863.14	1960.62	2038.03

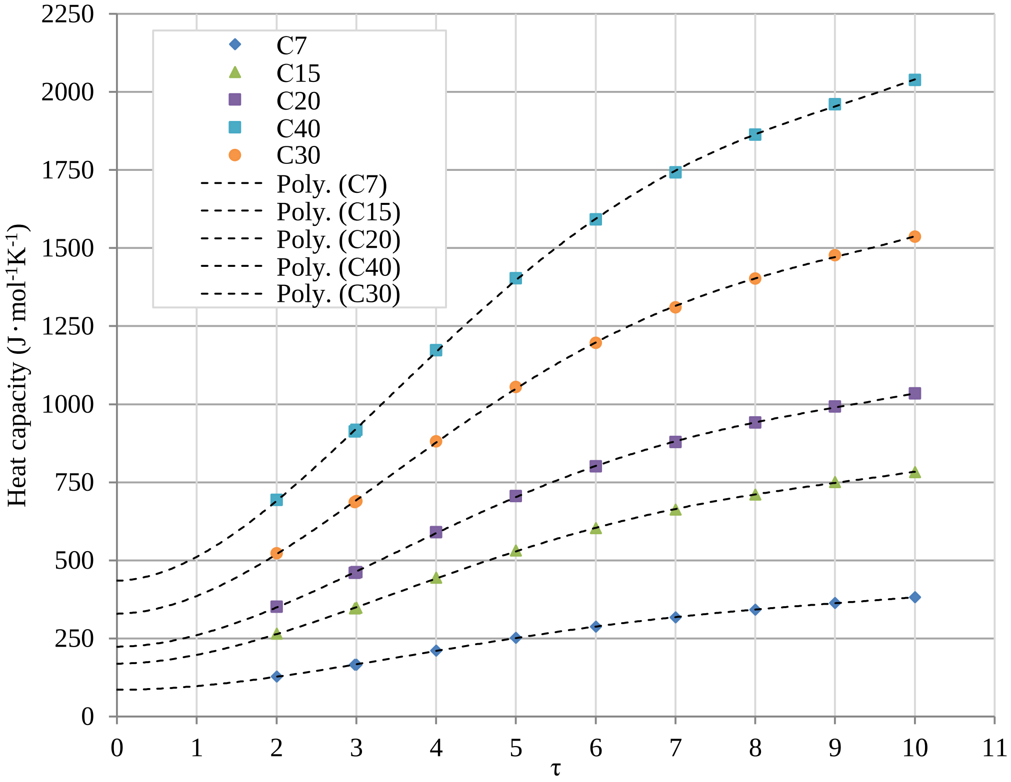

Figure 1 – Fitting the experimental data for c_p^{id} of n-alkanes C_7, C_{15}, C_{20}, C_{30}, C_{40}

Approximating the data from Table 1 with a third-degree polynomial fails to simultaneously describe the heat capacity of hydrocarbons accurately in both low- and high-temperature regions. However, switching to a fourth-degree polynomial enables reproduction of the inflection point observed in the 200–400 K range (Figure 1). Numerical calculation of the heat capacity derivative for *n*-heptane (Figure 2), using NIST database data, confirms this inflection point within the specified range. Consequently, a fourth-order polynomial was adopted for approximating thermodynamic properties in this study. For convenience, the reduced temperature parameter τ=T/100 was employed.

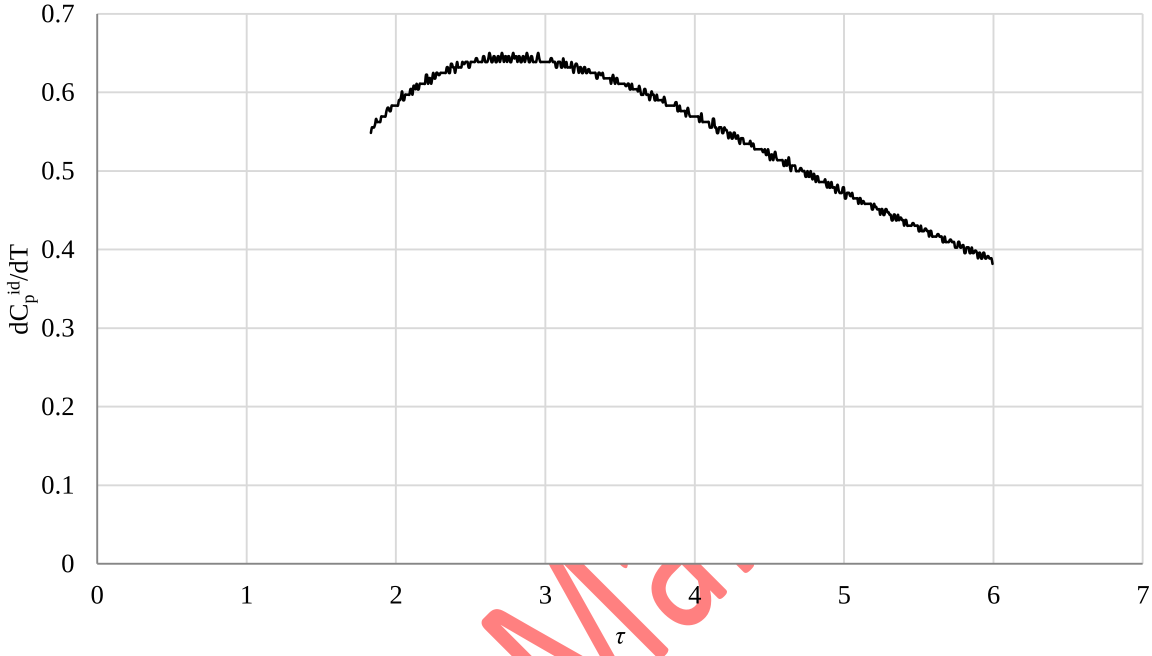

Figure 2 – Dependence of c_p^{id} /dT on τ for n-heptane

According to the regression analysis for hydrocarbons C_7 and C_8 the polynomials were found:

$$c_{p,n=7}^{id}(T) = 0.07\tau^4 - 1.79\tau^3 + 13.90\tau^2 - 0.37\tau + 85.43,$$
$$c_{p,n=8}^{id}(T) = 0.08\tau^4 - 2.04\tau^3 + 15.75\tau^2 + 0.30\tau + 95.59.$$

As noted in [26], due to the fact that alkanes C_n and C_{n+1} differ from each other by the radical CH_2, the increase in the carbon number by one leads to a linear dependence of the heat capacity on the number of carbon atoms $n$at constant temperature. In such a case, the linearization of the heat capacity can be written as:

$$c_{p,n}^{id}(T) = c_{p,n=7}^{id}(T) + f(T)(n - 7). \tag{5}$$

We define the function $f(T)$based on the approximation of *n*-hexane and *n*-octane

$$f(T) = c_{p,n=8}^{id}(T) - c_{p,n=7}^{id}(T) = 0.01\tau^4 - 0.25\tau^3 + 1.85\tau^2 + 0.66\tau + 10.16.$$

In most cases, technological processes involve hydrocarbon mixtures where the C_{7+} component composition is defined not by pure hydrocarbons but by petroleum fractions. These fractions are typically characterized in most software packages using two parameters: molecular weight (M_w) and liquid-phase specific gravity (SG). As shown in the Katz-Firoozabadi table [30], the relationship between a fraction molecular weight and its carbon number is nearly linear (Figure 3) and can be approximated by the expression:

$$M_w = 14.027n + 2.016. \tag{6}$$

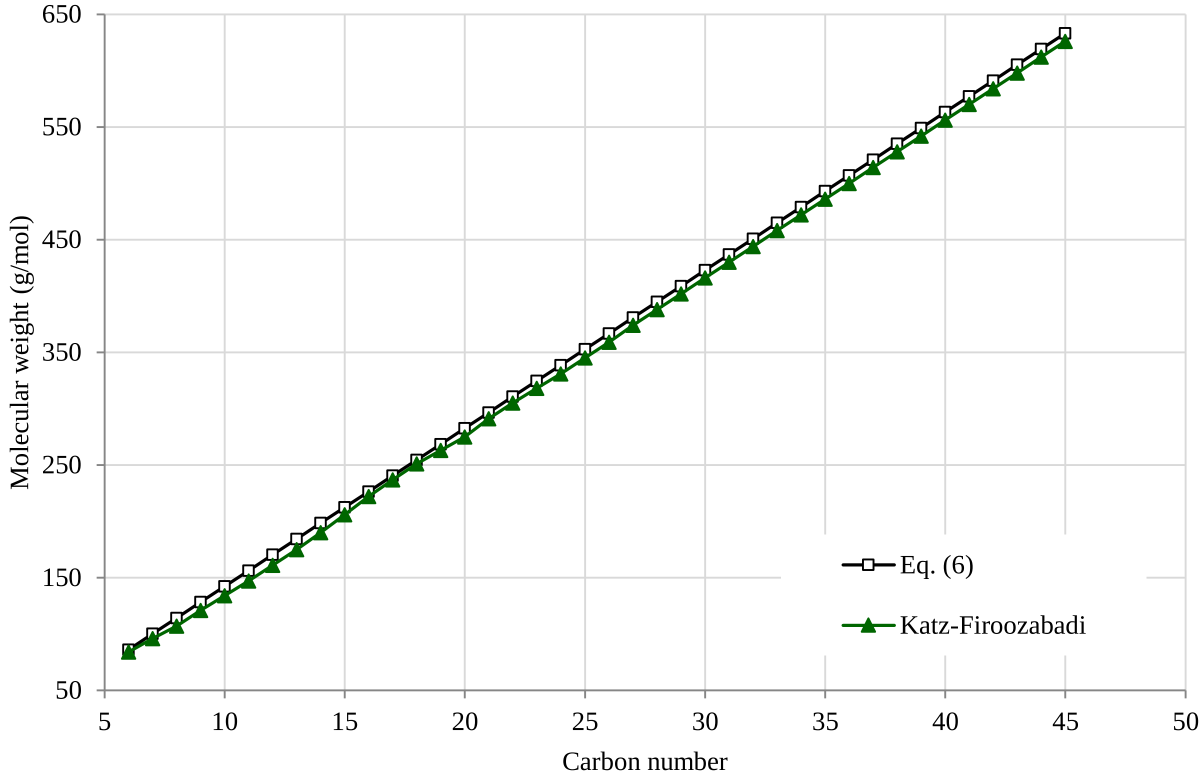

Figure 3 – Molecular weight of fraction C_n as a function of carbon number for pure alkanes and petroleum fractions

Combining equations (5) and (6) we obtain:

$$c_{p,n}^{id}(T) = c_{p,0}^{id}(T) + \alpha(T)M_w,$$

$$c_{p,0}^{id}(T) = -0.0002\tau^4 - 0.0017\tau^3 + 0.6835\tau^2 - 5.1153\tau + 12.8826, \tag{7}$$

$$\alpha(T) = 0.0007\tau^4 - 0.0179\tau^3 + 0.1319\tau^2 + 0.0474\tau + 0.724.$$

The extension of the Katz-Firoozabadi table to heavy components of C_{80}, proposed in [29], reveals a nonlinear relationship between molecular weight and the carbon number of the fraction. This dependence can be approximated using a second-order or higher polynomial. The functional relationship $M_w = M_w(n)$ may also serve as a modification of equation (6).

Enthalpy

According to thermodynamic relations, enthalpy for an ideal gas state can be determined from heat capacity as follows:

$$H_n^{id}(T) = \int_{T_1}^{T} c_{p,n}^{id}(T)dT + H_n^{id}(T_1).$$

Using expression (7) enthalpy can be expressed as:

$$H_n^{id}(T) = \int_{T_1}^{T} \left(c_{p,0}^{id}(T) + \alpha(T)M_w\right)dT + H_n^{id}(T_1). \qquad (8)$$

We choose $T_1 = 300$ K as a reference point. The integration constant is determined from linearization of experimental data from [31] (Table 2) through the values of n-heptane $H_7^{id}(T_1) = 32171$ J/mol and n-eicosane $H_{20}^{id}(T_1) = 86734$ J/mol:

$$H_n^{id}(T_1) = H_7^{id}(T_1) + (n-7)\frac{H_{20}^{id}(T_1) - H_7^{id}(T_1)}{13}.$$

Given the expression (6) the integration constant can be defined in terms of molecular weight:

$$H_n^{id}(T_1) = 299.22Mw + 2187.23. \qquad (9)$$

After integration of the fourth degree polynomials (7), the final expression for enthalpy calculation will be as follows:

$$H_n^{id}(T) = H_0^{id}(T) + \beta(T)Mw, \qquad (10)$$
$$H_0^{id}(T) = -0.004\tau^5 - 0.0425\tau^4 + 22.783\tau^3 - 255.765\tau^2 + 1288.26\tau + 13.6,$$
$$\beta(T) = 0.014\tau^5 - 0.4475\tau^4 + 4.3967\tau^3 + 2.37\tau^2 + 72.4\tau - 25.17,$$
$$\tau = \mathrm{T}/100.$$

Table 2 – Data used for fitting and testing enthalpy of petroleum fractions in the ideal gas state [31]

C_n	H_n^{id} (J/mol)							
	T (K)							
	300.0	400.0	500.0	600.0	700.0	800.0	900.0	1000.0
C_3	14836.5	23246.3	33639.4	45731.1	59371.0	74307.8	90374.4	107403.3
C_4	19618.8	30710.6	44329.5	60149.2	77906.1	97336.6	118202.2	140331.4
C_5	23773.5	37455.2	54266.5	73755.6	95596.0	119528.5	145163.9	172339.0
C_6	27978.4	44266.7	64266.2	87412.1	113373.8	141753.9	172200.9	204388.4
C_7	32170.8	51061.5	74245.1	101068.7	131122.4	164012.8	199237.9	236479.7
C_8	36363.1	57856.4	84223.9	114725.3	148870.9	186238.2	226274.9	268529.1
C_9	40568.1	64667.9	94223.7	128381.9	166619.4	208497.1	253274.3	300620.4
C_{10}	44752.1	71253.5	104202.5	142038.4	184397.2	230722.5	280311.3	332669.8

C11	48965.4	78257.5	114202.3	155695.0	202145.8	252947.9	307310.6	364719.3
C12	53157.7	85069.1	124181.1	169351.6	219894.3	275206.8	334347.6	396810.6
C13	57350.1	91863.9	134160.0	182983.1	237642.8	297423.8	361384.6	428860.0
C14	61555.0	98658.7	144159.7	196639.6	255391.4	319657.6	388384.0	460909.4
C15	65747.4	105453.5	154138.6	210296.2	273169.2	341883.0	415421.0	492958.9
C16	69952.3	112265.1	164138.3	223952.8	290917.7	364141.9	442420.3	525050.2
C17	74144.7	119059.9	174117.2	237609.4	308666.2	386367.3	469457.4	557099.6
C18	78337.0	125854.7	184096.0	251265.9	326414.8	408592.7	496494.4	589149.0
C19	82542.0	132666.3	194095.8	264922.5	344163.3	430851.6	523493.7	621240.3
C20	86734.3	139461.1	204062.0	278579.1	361941.1	453077.0	550530.7	653289.8

Entropy

Entropy for fluid in the ideal gas state can be obtained by integration of $c_{p,n}^{id}/T$

$$S_n^{id}(T) = \int_{T_1}^{T} \frac{c_{p,n}^{id}(T)}{T} dT + S_n^{id}(T_1).$$

The calculation procedure similar to those for enthalpy can be applied for entropy. Using the experimental data presented in table 3 and choosing as reference points the entropy values of *n*-heptane $S_7^{id}(T_1) = 429$ J/mol· K and *n*-eicosane $S_{20}^{id}(T_1) = 937$ J/mol· K formula for entropy calculation is as follows:

$$S_n^{id}(T) = S_0^{id}(T) + \gamma(T) M_w, \tag{11}$$

$$S_0^{id}(T) = -0.00005\tau^4 - 0.000566\tau^3 + 0.34175\tau^2 - 5.1153\tau + 12.8826\ln(\tau) + 147.7365,$$

$$\gamma(T) = 0.000175\tau^4 - 0.00596\tau^3 + 0.06595\tau^2 + 0.0474\tau + 0.724\ln(\tau) + 1.4028.$$

Table 3 – Data used for fitting and testing entropy of petroleum fractions in the ideal gas state [31]

Cn	S_n^{id} (J/mol· K)							
	T (K)							
	300.00	400.00	500.00	600.00	700.00	800.00	900.00	1000.00
C3	270.37	294.43	317.52	339.53	360.54	380.49	399.45	417.44
C4	310.66	342.71	373.21	402.12	429.53	455.51	480.07	503.38
C5	349.74	388.90	426.27	461.66	495.30	527.27	557.39	586.01
C6	389.36	435.97	480.45	522.50	562.50	600.36	636.18	670.11
C7	428.86	482.92	534.46	583.21	629.48	673.41	714.79	754.04
C8	467.94	529.44	588.10	643.50	696.09	746.01	792.95	837.55
C9	507.06	576.01	641.70	703.79	762.70	818.60	871.19	921.07
C10	546.14	622.54	695.34	764.08	829.27	891.15	949.43	1004.62
C11	585.22	669.11	748.98	824.37	895.88	963.74	1027.63	1088.13
C12	624.34	715.63	802.57	884.66	962.49	1036.33	1105.83	1171.65
C13	663.42	762.16	856.21	944.91	1029.10	1108.93	1184.03	1255.16
C14	702.49	808.73	909.85	1005.21	1095.71	1181.52	1262.23	1338.67
C15	741.57	855.25	963.49	1065.50	1162.27	1254.07	1340.47	1422.23

C_{16}	780.69	901.82	1017.09	1125.79	1228.88	1326.66	1418.67	1505.74
C_{17}	819.77	948.35	1070.73	1185.87	1295.53	1399.26	1496.87	1589.25
C_{18}	858.85	994.87	1124.37	1246.37	1362.06	1471.85	1575.07	1672.76
C_{19}	897.97	1041.44	1177.96	1306.66	1428.71	1544.44	1653.27	1756.28
C_{20}	937.05	1087.97	1231.60	1366.95	1495.28	1616.99	1731.51	1839.83

Results and discussions

Based on 340 experimental values of c_p^{id} for pure alkanes from C_7 to C_{40}, a comparison of different methods to predict the heat capacity in the ideal gas state has been made. For enthalpy and entropy estimation, data from 112 experimental points from [31] were used (Tables 1-3). The accuracy of various correlations was evaluated using stochastic parameters: AARE, MARE, MSE, RMSE, SD, R^2 [32].

$$AARE = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{c_{p,i}^{id,cal} - c_{p,i}^{id,exp}}{c_{p,i}^{id,exp}}\right| \times 100\%,$$

$$MARE = \max_{i}\left\{\left|\frac{c_{p,i}^{id,cal} - c_{p,i}^{id,exp}}{c_{p,i}^{id,exp}}\right| \times 100\%\right\},$$

$$MSE = \frac{1}{N}\sum_{i=1}^{N}\left(c_{p,i}^{id,cal} - c_{p,i}^{id,exp}\right)^2,$$

$$RMSE = \sqrt{\frac{1}{N}\sum_{i=1}^{N}\left(c_{p,i}^{id,cal} - c_{p,i}^{id,exp}\right)^2},$$

$$SD = \sqrt{\frac{1}{N-1}\sum_{i=1}^{N}\left(c_{p,i}^{id,cal} - average\left(c_{p,i}^{id,exp}\right)\right)^2},$$

$$R^2 = 1 - \frac{\sum_{i=1}^{N}\left(c_{p,i}^{id,cal} - c_{p,i}^{id,exp}\right)^2}{\sum_{i=1}^{N}\left(c_{p,i}^{id,cal} - average\left(c_{p,i}^{id,exp}\right)\right)^2},$$

The results of heat capacity calculation using different methods are presented in tables 4-5 and figures 4-5 (C_n will refer to n-alkanes with the formula C_nH_{2n+2}).

Table 4. Comparison of different correlations for heat capacity in the ideal gas state calculation in the temperature range 200-1000 K.

C_n	NPTS	AARE, %					MARE, %				
		Huang, 2019	Lee-Kesler, 1976	Lee-Kesler2, 1976	Kuznetsov, 2021	Eq. (7)	Huang, 2019	Lee-Kesler, 1976	Lee-Kesler2, 1976	Kuznetsov, 2021	Eq. (7)
C_7	10	2.07	2.48	1.53	1.29	0.70	8.28	6.97	6.30	9.20	1.49
C_8	10	1.82	2.44	1.52	1.30	0.71	7.81	7.09	6.45	8.83	1.52
C_9	10	1.62	2.18	1.66	1.32	0.71	7.45	7.72	7.05	8.56	1.63

C_{10}	10	1.49	2.90	1.10	1.35	0.75	7.16	6.37	5.71	8.34	1.71
C_{11}	10	1.37	2.69	1.22	1.37	0.78	6.93	6.77	6.12	8.16	1.79
C_{12}	10	1.27	2.94	1.13	1.40	0.80	6.73	6.32	5.67	8.01	1.85
C_{13}	10	1.20	3.30	1.20	1.42	0.83	6.56	6.47	4.99	7.88	1.90
C_{14}	10	1.10	3.64	1.31	1.39	0.83	6.42	7.08	4.26	7.77	1.95
C_{15}	10	1.12	4.06	1.52	1.44	0.86	6.29	7.62	3.60	7.68	1.98
C_{16}	10	1.15	4.88	2.10	1.47	0.86	6.18	8.60	3.63	7.59	2.02
C_{17}	10	1.16	4.79	2.07	1.48	0.88	6.08	8.64	3.51	7.52	2.05
C_{18}	10	1.15	5.83	2.69	1.48	0.90	5.99	9.76	4.94	7.45	2.08
C_{19}	10	1.18	5.51	2.55	1.49	0.90	5.91	9.54	4.50	7.39	2.10
C_{20}	10	1.22	5.89	2.74	1.51	0.90	5.84	9.98	5.00	7.34	2.12
C_{21}	10	1.25	6.24	3.02	1.51	0.91	5.78	10.38	5.47	7.29	2.14
C_{22}	10	1.27	6.62	3.33	1.52	0.92	5.72	10.79	5.97	7.24	2.16
C_{23}	10	1.30	6.95	3.59	1.53	0.93	5.66	11.14	6.41	7.20	2.18
C_{24}	10	1.32	7.32	3.85	1.53	0.93	5.62	11.49	6.88	7.16	2.19
C_{25}	10	1.34	7.65	4.07	1.54	0.94	5.57	11.81	7.31	7.13	2.21
C_{26}	10	1.36	7.98	4.27	1.55	0.94	5.53	12.10	7.72	7.10	2.22
C_{27}	10	1.38	9.63	4.94	1.55	0.95	5.49	13.21	9.57	7.07	2.23
C_{28}	10	1.40	8.66	4.63	1.55	0.95	5.45	12.65	8.54	7.04	2.24
C_{29}	10	1.42	9.15	4.84	1.56	0.95	5.42	12.99	9.08	7.01	2.25
C_{30}	10	1.44	8.70	4.69	1.56	0.96	5.39	12.72	8.59	6.99	2.26
C_{31}	10	1.46	9.00	4.83	1.57	0.96	5.36	12.94	8.94	6.97	2.27
C_{32}	10	1.47	9.36	4.98	1.57	0.97	5.33	13.18	9.34	6.95	2.28
C_{33}	10	1.49	9.60	5.08	1.57	0.97	5.30	13.34	9.63	6.93	2.29
C_{34}	10	1.50	9.96	5.20	1.58	0.97	5.28	13.57	10.04	6.91	2.30
C_{35}	10	1.51	10.23	5.30	1.58	0.97	5.26	13.73	10.35	6.89	2.30
C_{36}	10	1.53	10.49	5.38	1.58	0.98	5.23	13.89	10.66	6.87	2.31
C_{37}	10	1.54	10.80	5.47	1.59	0.98	5.21	14.07	11.02	6.86	2.32
C_{38}	10	1.55	11.07	5.53	1.59	0.98	5.20	14.22	11.34	6.84	2.32
C_{39}	10	1.56	11.25	5.58	1.59	0.98	5.18	14.32	11.56	6.83	2.33
C_{40}	10	1.57	11.50	5.63	1.60	0.99	5.16	14.48	11.85	6.82	2.33
Average	**340**	**1.40**	**6.93**	**3.49**	**1.50**	**0.90**	**5.93**	**10.76**	**7.41**	**7.41**	**2.10**

[a] NPTS is the number of points considered

Table 5. Average error values for heat capacity calculation of hydrocarbons C_7-C_{40} in the ideal gas state in the temperatures range 200-1000 K.

	AARE, %	MARE, %	MSE	RMSE	SD	R^2
Huang, 2019	1.40	5.93	157.03	11.41	291.84	1.00
Lee-Kesler, 1976	6.93	10.76	10817.18	85.84	340.56	0.94
Lee-Kesler2, 1976	3.49	7.41	1488.90	32.06	288.00	0.99
Kuznetsov, 2021	1.50	7.41	242.32	14.15	295.85	1.00
Eq. (7)	0.90	2.10	180.93	12.17	279.45	1.00

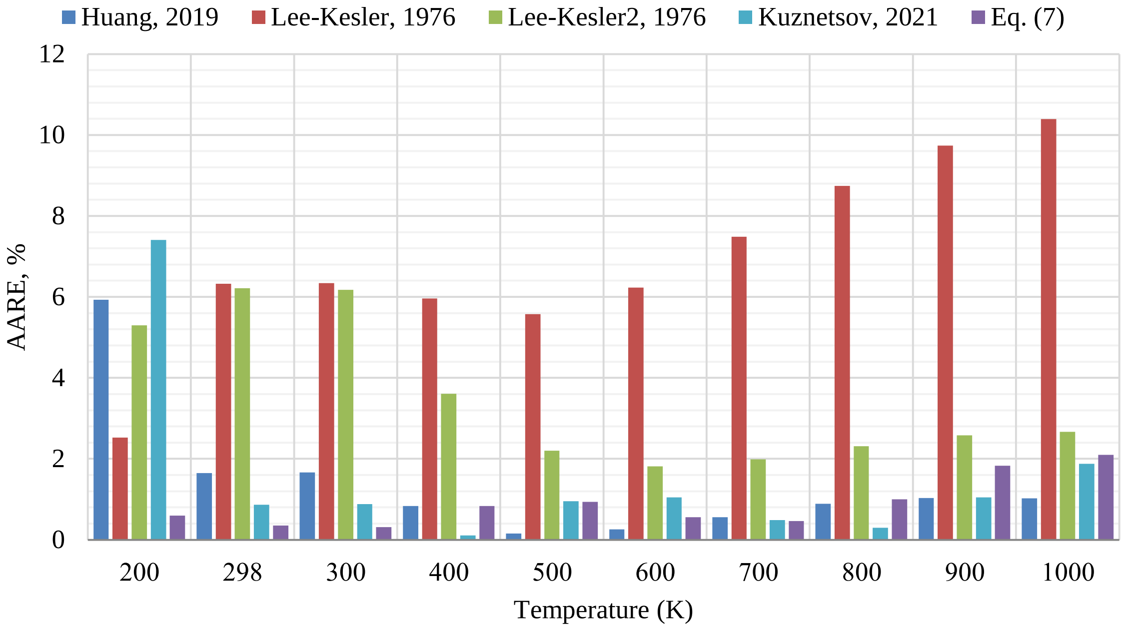

Figure 4 – AARE for experimental and computational methods of heat capacity for hydrocarbons from C_7 to C_{40}.

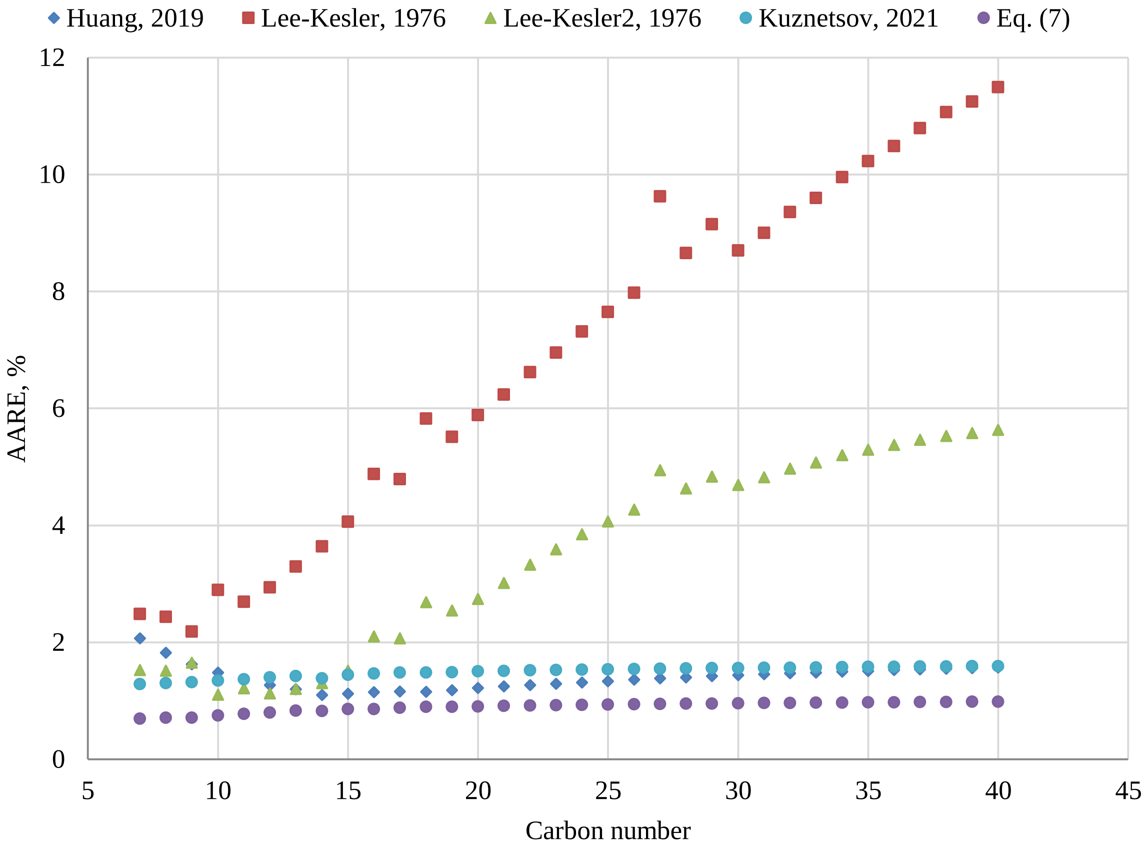

Figure 5 – AARE depending on the carbon number for c_p^{id} of *n*-alkane

It should be noted that the best results are achieved using the method proposed by correlation (7), along with equations (3) and (4) [25-26]. Due to the derivation methodology of correlation (4), the maximum calculation error occurs in the low-temperature region, as the formula was originally developed for the temperature range of 300–1500 K. Similarly, formula (3) shows its largest discrepancies at low temperatures.

It is important to mention that the temperature range of 200–300 K represents typical operating conditions for surface facilities in well production gathering and treatment systems at oil, gas, and condensate fields and should also be accounted for when developing correlations. Cross-plot comparisons between calculated and experimental data (Figure 6) clearly demonstrate the limitations of equations (3) and (4) in this low-temperature region.

Significant deviations in the Kesler-Lee correlation are related to the specifics of its derivation, as it was based on experimental data for light and medium paraffin compounds. The proposed correlation (7) in this study reduces the values of the AARE, MARE, and RMSE parameters compared to the Kesler-Lee correlation—from 6.93%, 10.76%, and 85.84 to 0.90%, 2.10%, and 12.17, respectively.

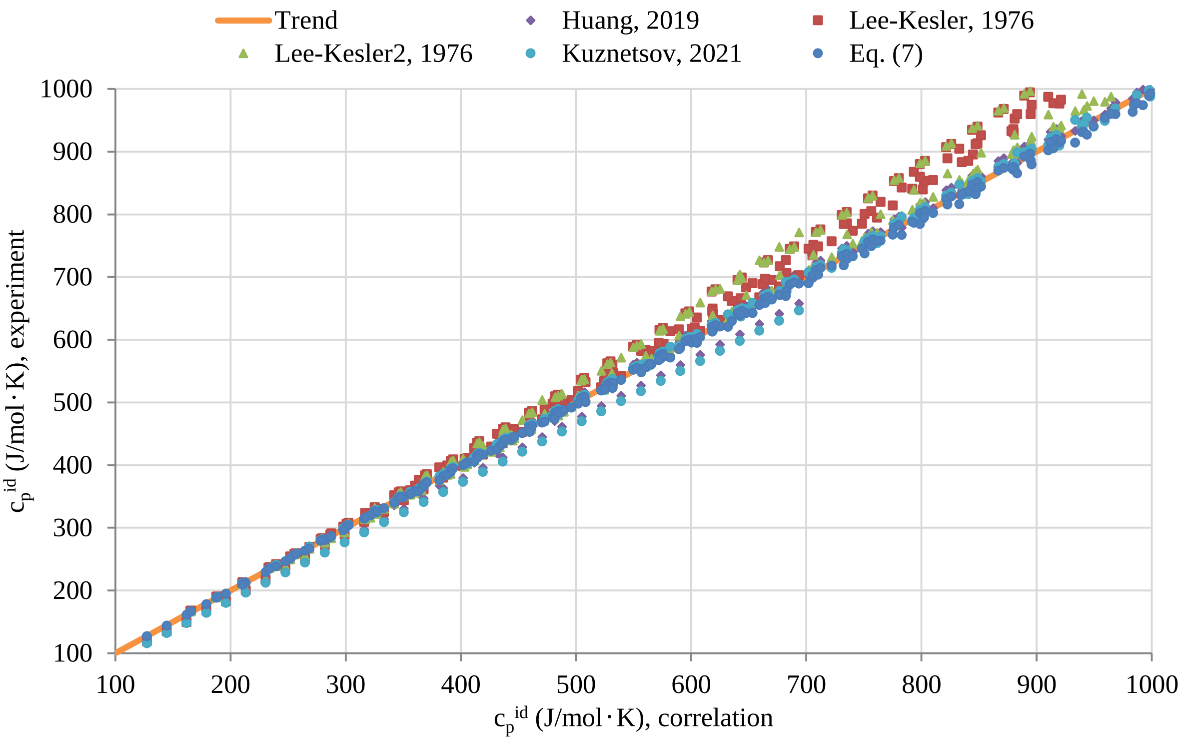

Figure 6 – Cross-plot for different correlations

For independent verification, the presented correlations were tested against the data provided in Table 6.

Table 6 – Data for model verification

Formula	Formula	NPTS	Temperature range, K	Ref
C_7H_{16}	n-Heptane	42	182.55-600	[33]
		1	298.15	[34]
C_8H_{18}	n-Octane	52	216.37-730	[33]
C_9H_{20}	n-Nonane	39	219.7-600	[33]
$C_{10}H_{22}$	n-Decane	44	243.5-675	[33]
$C_{12}H_{26}$	n-Dodecane	44	263.6-700	[33]

Results of statistical analysis are shown in table 7.

Table 7 – Results of statistical analysis for isobaric heat capacity of n-alkanes in the ideal gas state

C_n	Huang, 2019	Lee-Kesler, 1976	Lee-Kesler2, 1976	Kuznetsov, 2021	Eq. (7)
AARE, %					
C_7	1.530	1.927	1.337	1.559	0.534
C_8	1.067	1.182	1.215	0.994	0.530
C_9	0.571	0.463	0.917	0.609	0.391
C_{10}	0.512	1.042	0.665	0.541	0.438
C_{12}	0.474	1.022	0.707	0.533	0.468
MARE, %					
C_7	13.010	11.564	10.679	14.228	2.501
C_8	6.082	5.494	5.045	6.862	0.913
C_9	4.153	4.532	4.129	4.997	0.774
C_{10}	1.335	2.216	1.138	2.012	0.800
C_{12}	1.319	2.470	1.248	0.909	0.863
MSE					
C_7	17.762	18.738	11.743	20.869	1.376
C_8	11.608	12.199	15.551	9.385	2.358
C_9	5.145	4.119	17.696	6.295	2.371
C_{10}	4.419	21.277	9.143	5.369	3.258
C_{12}	5.268	33.903	15.598	8.607	5.706
RMSE					
C_7	4.214	4.329	3.427	4.568	1.173
C_8	3.407	3.493	3.944	3.064	1.535
C_9	2.268	2.030	4.207	2.509	1.540
C_{10}	2.102	4.613	3.024	2.317	1.805
C_{12}	2.295	5.823	3.949	2.934	2.389
SD					
C_7	52.106	53.542	51.151	52.838	50.178
C_8	65.920	69.192	65.392	66.638	66.234
C_9	60.236	61.946	59.176	60.553	59.599
C_{10}	70.695	74.095	70.012	70.856	71.394
C_{12}	82.348	86.747	81.715	82.184	83.557
R2					
C_7	0.993	0.993	0.995	0.992	0.999
C_8	0.997	0.997	0.996	0.998	0.999
C_9	0.999	0.999	0.995	0.998	0.999
C_{10}	0.999	0.996	0.998	0.999	0.999
C_{12}	0.999	0.995	0.998	0.999	0.999

The obtained results demonstrate that the proposed correlation (Eq. 7) provides the highest accuracy for calculating the isobaric heat capacity of *n*-alkanes in the ideal gas state. To extend the correlation applicability to broader hydrocarbon classes (cycloalkanes and aromatic hydrocarbons), experimental data from [32] for the temperature range 298.15 – 1000 K were considered. The results of the heat capacity discrepancies for various correlations are presented in tables 8-9.

Table 8 – Results of the statistical analysis of the isobaric heat capacity of cycloalkanes in the ideal gas state

Name	Huang, 2019	Lee-Kesler, 1976	Lee-Kesler2, 1976	Eq. (7)
	AARE, %			
Methylcyclopentane	12.501	3.321	16.057	13.451
Cyclohexane	11.589	6.634	11.940	12.080
Cis-1,3-Dimethylcyclopentane	9.327	2.126	10.662	9.665
Trans-1,3-Dimethylcyclopentane	9.327	2.126	10.662	9.665
Trans-1,2-Dimethylcyclopentane	9.327	2.140	9.123	9.665
Methylcyclohexane	7.465	4.460	9.236	7.342
Ethylcyclopentane	10.595	2.412	8.563	10.937
1,1-Dimethylcyclohexane	7.384	4.903	8.489	7.181
Ethylcyclohexane	6.221	3.917	7.646	6.022
Average	**9.304**	**3.560**	**10.264**	**9.557**
	MARE, %			
Methylcyclopentane	26.952	7.516	25.997	27.411
Cyclohexane	31.150	12.024	19.943	31.624
Cis-1,3-Dimethylcyclopentane	20.922	4.996	18.042	20.907
Trans-1,3-Dimethylcyclopentane	20.922	4.996	18.042	20.907
Trans-1,2-Dimethylcyclopentane	20.922	5.094	14.998	20.907
Methylcyclohexane	20.435	8.953	18.004	20.419
Ethylcyclopentane	23.418	5.495	13.277	23.402
1,1-Dimethylcyclohexane	20.369	9.554	16.469	20.016
Ethylcyclohexane	17.008	7.925	16.025	16.665
Average	**22.455**	**7.395**	**17.866**	**22.473**
	MSE			
Methylcyclopentane	461.216	44.225	1976.847	542.338
Cyclohexane	409.683	398.560	1163.364	432.560
Cis-1,3-Dimethylcyclopentane	375.331	31.069	1274.450	401.791
Trans-1,3-Dimethylcyclopentane	375.331	31.069	1274.450	401.791
Trans-1,2-Dimethylcyclopentane	375.331	30.721	886.155	401.791
Methylcyclohexane	264.379	294.897	1228.578	256.312
Ethylcyclopentane	473.505	47.713	728.796	506.736
1,1-Dimethylcyclohexane	343.651	469.246	1332.976	318.781
Ethylcyclohexane	250.735	313.882	1231.257	231.498
Average	**369.907**	**184.598**	**1232.986**	**388.177**
	RMSE			
Methylcyclopentane	21.476	6.650	44.462	23.288
Cyclohexane	20.241	19.964	34.108	20.798
Cis-1,3-Dimethylcyclopentane	19.373	5.574	35.699	20.045
Trans-1,3-Dimethylcyclopentane	19.373	5.574	35.699	20.045
Trans-1,2-Dimethylcyclopentane	19.373	5.543	29.768	20.045
Methylcyclohexane	16.260	17.173	35.051	16.010
Ethylcyclopentane	21.760	6.907	26.996	22.511
1,1-Dimethylcyclohexane	18.538	21.662	36.510	17.854
Ethylcyclohexane	15.835	17.717	35.089	15.215
Average	**19.137**	**11.863**	**34.820**	**19.534**
	SD			
Methylcyclopentane	69.586	66.992	105.804	72.778
Cyclohexane	68.057	65.966	103.920	71.107
Cis-1,3-Dimethylcyclopentane	79.513	79.240	109.360	81.463
Trans-1,3-Dimethylcyclopentane	79.513	79.240	109.360	81.463
Trans-1,2-Dimethylcyclopentane	79.513	79.280	104.234	81.463
Methylcyclohexane	78.021	78.835	115.566	79.879
Ethylcyclopentane	80.182	78.239	101.877	82.159
1,1-Dimethylcyclohexane	88.927	90.267	130.172	89.807
Ethylcyclohexane	88.879	90.448	126.860	89.759
Average	**79.132**	**78.723**	**111.906**	**81.098**

Table 9 – Results of the statistical analysis of the isobaric heat capacity of aromatic hydrocarbons in the ideal gas state

Name	Huang, 2019	Lee-Kesler, 1976	Lee-Kesler2, 1976	Eq. (7)
	AARE, %			
Benzene	44.449	1.838	6.118	46.476
Toluene	36.814	3.656	1.624	37.877
Ethylbenzene	29.540	1.855	1.307	29.952
n-xylene	31.821	4.947	4.687	32.237
m-xylene	31.104	3.887	3.273	31.519
o-xylene	28.935	2.829	1.966	29.353
Styrene	36.963	3.817	1.871	37.492
Cumene	24.927	1.772	1.898	24.879
Average	**33.069**	**3.075**	**2.843**	**33.723**
	MARE, %			
Benzene	58.266	2.956	10.223	59.286
Toluene	46.940	5.049	2.528	47.256
Ethylbenzene	36.815	3.670	2.729	36.677
n-xylene	38.485	6.588	6.107	38.345
m-xylene	37.713	5.680	4.676	37.574
o-xylene	31.833	5.495	5.557	31.700
Styrene	41.160	6.613	3.581	41.075
Cumene	31.093	3.071	3.837	30.643
Average	**40.288**	**4.890**	**4.905**	**40.320**
	MSE			
Benzene	4099.081	11.612	167.629	4657.682
Toluene	4369.442	67.195	8.644	4767.004
Ethylbenzene	4212.719	43.506	22.626	4436.271
n-xylene	4728.561	173.308	151.734	4963.038
m-xylene	4575.847	122.579	82.009	4807.439
o-xylene	4281.519	42.609	16.820	4512.379
Styrene	6055.542	120.660	13.717	6364.818
Cumene	4128.665	41.392	61.789	4186.187
Average	**4556.422**	**77.858**	**65.621**	**4836.852**
	RMSE			
Benzene	64.024	3.408	12.947	68.247
Toluene	66.102	8.197	2.940	69.043
Ethylbenzene	64.905	6.596	4.757	66.605
n-xylene	68.765	13.165	12.318	70.449
m-xylene	67.645	11.072	9.056	69.336
o-xylene	65.433	6.528	4.101	67.174
Styrene	77.817	10.985	3.704	79.780
Cumene	64.255	6.434	7.861	64.701
Average	**67.368**	**8.298**	**7.210**	**69.417**
	SD			
Benzene	90.421	50.541	57.724	95.517
Toluene	99.631	63.925	59.750	103.355
Ethylbenzene	106.924	75.013	73.704	109.315
n-xylene	109.524	76.606	76.028	111.913
m-xylene	108.747	76.011	74.541	111.136
o-xylene	106.940	74.164	71.144	109.331
Styrene	114.134	71.173	65.409	116.702
Cumene	115.210	86.545	87.582	116.330
Average	**106.441**	**71.747**	**70.735**	**109.200**

Figure 7-8 shows histograms of the AARE parameter change in heat capacity calculations for cycloalkanes and aromatic hydrocarbons in the ideal gas state.

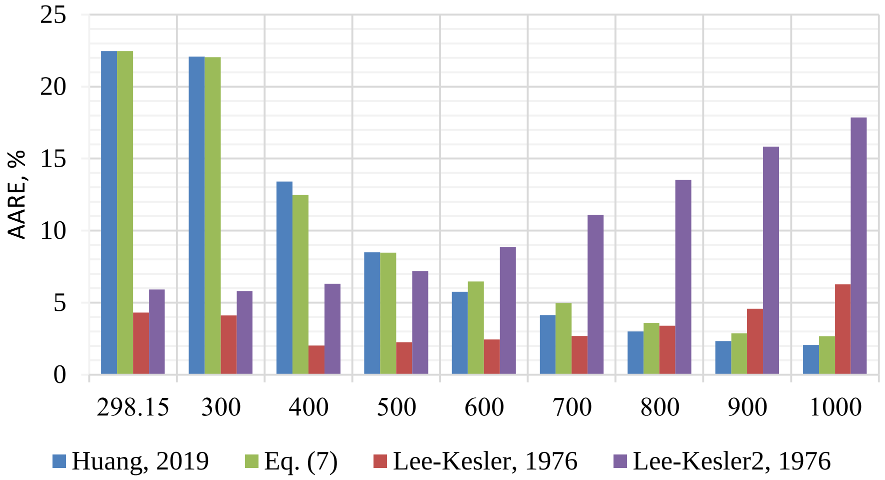

Figure 7 – AARE values for heat capacity calculations of cycloalkanes

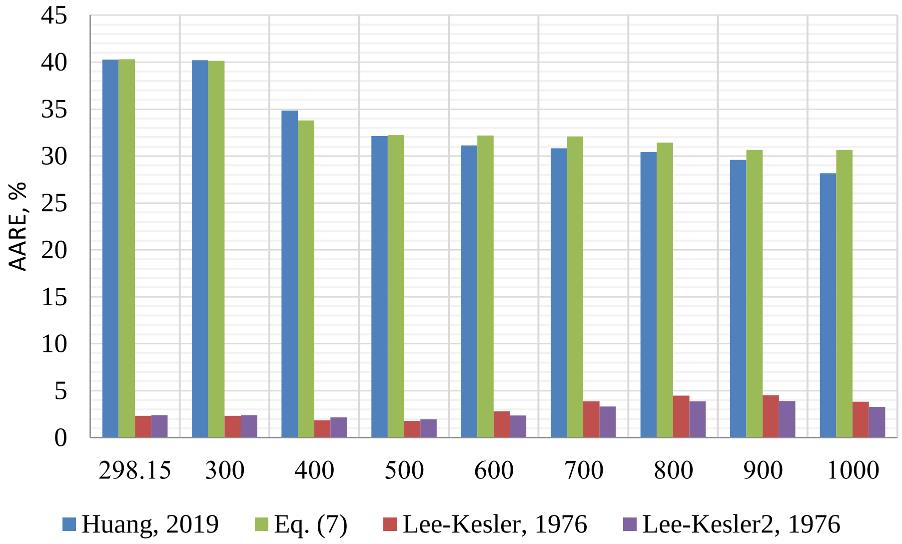

Figure 8 – AARE values for heat capacity calculations of aromatic hydrocarbons

As previously noted, due to the specifics of the Kesler-Lee correlation derivation for light hydrocarbon fractions, correlations (7) and (3) are significantly less accurate for such compounds. Figure 9 shows the dependence of the heat capacity estimation error on molecular weight according to equation (7), demonstrating improved accuracy with increasing molecular weight.

Therefore, the proposed correlation (7) demonstrates reliable accuracy for n-alkanes within the 200–1000 K temperature range. However, application to pure naphthenic and aromatic compounds requires caution due to significant deviations observed in light fractions. Future incorporation of the specific gravity parameter into equation (7) may resolve these discrepancies.

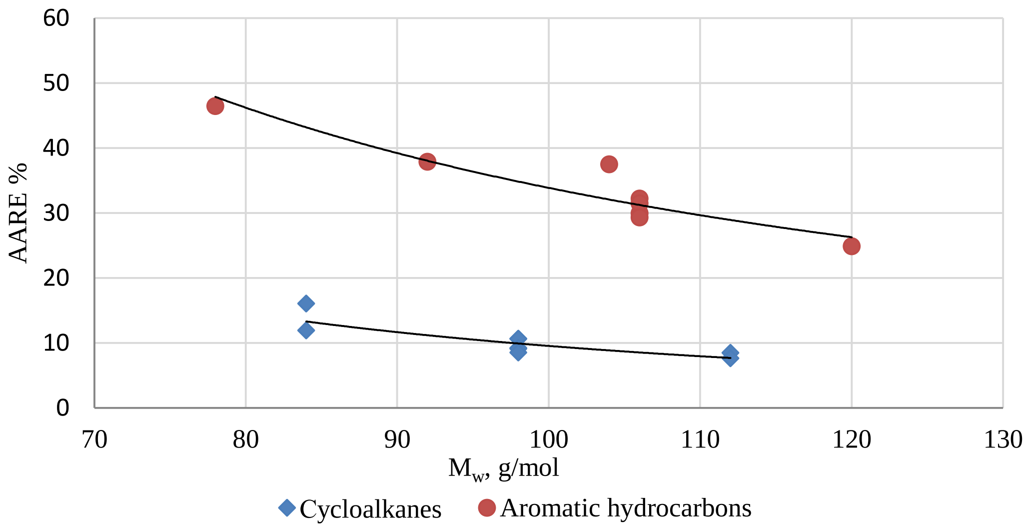

Figure 9 – The dependence of the heat capacity estimation error on molecular weight

According to experimental data (Tables 2-3) for hydrocarbons C_7-C_{20}, the equations (10) and (11) allow one to calculate enthalpy and entropy values with AARE not exceeding 0.3% and 0.1%, respectively. The variation of AARE from the carbon number of *n*-alkane is shown in Figure 10. As enthalpy and entropy depend on heat capacity, the maximum errors are observed at high temperatures close to 1000 K. Similarly to heat capacity, the obtained correlation models can be used both for heavier hydrocarbon fractions and for light components down to butane.

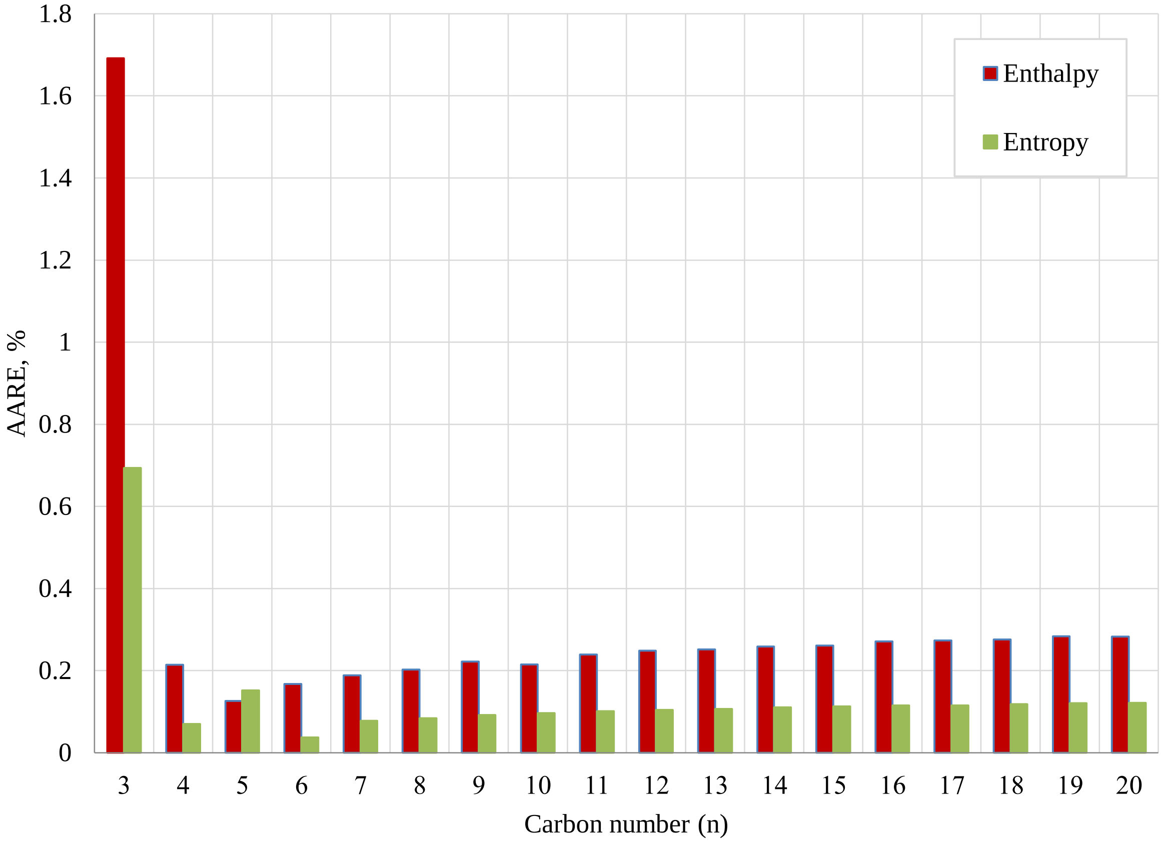

Figure 10 – AARE for enthalpy *H* and entropy *S* of n-alkanes.

Conclusion

In this study, a new empirical correlation for calculating the thermodynamic properties of hydrocarbons in the ideal gas state has been developed. A comparative analysis with existing methods revealed that the proposed model provides high accuracy, particularly in the low-temperature range (200–300 K), making it suitable for oil, gas, and gas condensate collection and processing systems.

In contrast to traditional methods, the proposed correlation accounts for both temperature dependence and structural characteristics of heavy hydrocarbon fractions, significantly reducing calculation errors compared to the Kesler-Lee model and other correlations for n-alkanes. The model's reliability has been validated through experimental data comparisons and accuracy assessments using statistical metrics. The correlation developed in this work demonstrates a significant reduction in AARE and MARE values compared to the Kesler-Lee correlation from 6.93% and 10.76% to 0.90% and 2.10% respectively. For naphthenic and aromatic compounds, this correlation remains applicable though with higher uncertainty.

The obtained results can be utilized for more precise thermodynamic modeling in the oil and gas industry, as well as for the development of new hydrocarbon processing and transportation methods. Future research includes adapting the proposed correlation for multicomponent mixtures and integrating it into modern software for PVT analysis.

Nomenclatures

M_w	Molecular weight	[g/mol]
T	Temperature	[K]
T_b	Boiling temperature	[K]
SG	Specific gravity	[-]
c_p^{id}	Heat capacity in the ideal gas state	[J/mol□K]
H_n^{id}	Enthalpy in the ideal gas state	[J/mol]
S_n^{id}	Entropy in the ideal gas state	[J/ mol□K]
K_W	Watson characterization factor	[-]
C_0, C_1, C_2	Coefficients	[-]
A_0, A_1, A_2	Coefficients	[-]
B_0, B_1, B_2	Coefficients	[-]
C_{F0}, C_F	Coefficient	[-]
N	Number of components	
τ	Reduced temperature	
Greek symbols		
ω	Acentric factor	[-]
Subscripts and indices		
n	Carbon number	[-]
P_c	Critical pressure	[bar]
T_c	Critical temperature	[K]
T_{br}	T_b/T_c,	

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