

# A New Group-Contribution Method for the Estimation of Physical Properties of Hydrocarbons

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**Résumé — Nouvelle méthode de contribution de groupes pour l'estimation des propriétés physiques des hydrocarbure** — Dans le présent article, nous proposons une nouvelle méthode de contribution de groupes pour l'estimation de la température d'ébullition, du point de congélation et de la densité liquide à 20 °C des hydrocarbures purs. La méthode a été établie avec une assez bonne précision et, comparée à d'autres méthodes de contributions de groupes, elle a enregistré de meilleurs résultats en termes de déviations standard moyennes.

**Abstract — A New Group-Contribution Method for the Estimation of Physical Properties of Hydrocarbons** — In the present work, we propose a new group-contribution method to estimate the boiling point, freezing point and the liquid density at 20°C of hydrocarbons. The method was tested with satisfactory accuracy, and when compared with other group-contribution methods, it reveals better results in terms of average standard deviations.

## NOTATIONS

$a, b, c, d, m, n, p$  constants for each property in Equation F  
 $d_{20}$  liquid density at 20°C (kg/m<sup>3</sup>)  
 $F$  mathematical function  
 $M$  molecular weight (g/mol)  
 $T_b$  normal boiling point (K)  
 $T_F$  freezing point (K).

## Greek letters

$\theta$  a given property  
 $\Delta\theta_i$  contribution of the group  $i$  for the evaluation of the property  $\theta$ .

## INTRODUCTION

Physical properties of hydrocarbons are required in the design of most petroleum processing equipments. These characteristics can be obtained through experimental measurements, graphical methods or analytical equations. The most widely used are those of group-contribution methods such those of Lydersen (1955), Joback (1984), Ambrose (1980), Klincewicz and Reid (1984), Constantinou *et al.* (1994), Constantinou *et al.* (1995), which are based only on the molecular structure of the compound. The property is estimated by a summation of the contributions of individual groups and fragments which constitute the molecule. Even if these correlations are able to estimate the

properties quite rapidly, many of them fail in distinguishing among isomers due to the oversimplification of the molecule structure or, in extrapolating to heavier compounds.

In this work, we have proposed a group-contribution method which allows to capture isomers differences to estimate boiling point (K), freezing point (K) and liquid density at 20°C (kg/m<sup>3</sup>) of pure hydrocarbons. The average absolute deviations of the new correlations are 0.77%, 8.44% and 1.30% respectively for boiling point, freezing point and density.

## 1 PROPOSED METHOD

This work was carried out on the basis of a compiled properties values of pure compounds, obtained exclusively from the TRC data bank (TRC, Thermodynamic Data Base, version 1.3, 1994). The study concerns only hydrocarbons belonging to the following families: *n*-paraffins, iso-paraffins, olefins, alcyne, naphthenes and aromatics, because of their predominance in petroleum industry. Condensed rings are not considered in this work, an extension of the present work to these types of molecules will be done in the future.

On the basis of the molecule's structures of the data bank compounds, we selected first 10 types of groups: CH<sub>3</sub>, CH<sub>2</sub>, CH, C, =CH<sub>2</sub>, =CH, =C, =C=, ≡CH and ≡C, without any distinction between aliphatic and ring chains. Therefore, we admit at first sight that each group has a single contribution when appearing in a paraffinic, naphthenic or aromatic molecule. Then, a set of 42 other groups was added to distinguish between the different families and also between isomers whether in aliphatic or ring structures. In developing these correction groups, we take into account the proximity effects of the CH<sub>3</sub> groups. In the same way, we affect correction terms to saturated rings in naphthenes and to the benzene ring, in addition to those of the position *cis*- and *trans*- in olefinic and naphthenic molecules, and *ortho*, *meta*, *para* and other *tri*- and *tetra*-substituted positions.

After generating the group additivity parameters, we proceed to the analysis of the data from the experimental values of boiling point (K), freezing point (K) and liquid density (kg/m<sup>3</sup>).

To develop a group additivity relationship, we try several equations which can be generalised in mathematical form by the following relationship:

$$F(\theta) = a + b \Sigma \Delta \theta_i + c (\Sigma \Delta \theta_i)^m + d (\Sigma \Delta \theta_i)^n$$

where  $\theta$  is a given property and  $F(\theta)$  a function equal to  $\theta$ ,  $\exp(\theta/p)$ ,  $1/\theta^p$ ,  $M/\theta$  or  $T_b/\theta$ . The parameters  $a$ ,  $b$ ,  $c$ ,  $d$ ,  $m$ ,  $n$  and  $p$  are constants determined by the regression.  $T_b$  (K) and  $M$ (g/mol) are respectively the boiling point and the molecular weight.

Twenty equations can be derived from the generalised equation according to the shape of the function  $F$  and by cancelling one or several parameters in the expression of the generalised correlation, like shown in Table 1. The aim of this approach is to test different forms of mathematical equations to provide the best correlation with the minimum error.

TABLE 1

The different forms of Equation F( $\theta$ )

Equation (1)	$\theta = b * \Sigma \Delta \theta_i$
Equation (2)	$\exp(\theta/p) = b * \Sigma \Delta \theta_i$
Equation (3)	$(1/\theta)^p = b * \Sigma \Delta \theta_i$
Equation (4)	$(M/\theta) = b * \Sigma \Delta \theta_i$
Equation (5)	$(T_b/\theta) = b * \Sigma \Delta \theta_i$
Equation (6)	$\theta = a + b * \Sigma \Delta \theta_i$
Equation (7)	$\exp(\theta/p) = a + b * \Sigma \Delta \theta_i + c (\Sigma \Delta \theta_i)^m$
Equation (8)	$(1/\theta)^p = a + b * \Sigma \Delta \theta_i$
Equation (9)	$(M/\theta) = a + b * \Sigma \Delta \theta_i$
Equation (10)	$(T_b/\theta) = a + b * \Sigma \Delta \theta_i$
Equation (11)	$\theta = a + b * \Sigma \Delta \theta_i + c (\Sigma \Delta \theta_i)^m$
Equation (12)	$\exp(\theta/p) = a + b * \Sigma \Delta \theta_i + c (\Sigma \Delta \theta_i)^m$
Equation (13)	$(1/\theta)^p = a + b * \Sigma \Delta \theta_i + c (\Sigma \Delta \theta_i)^m$
Equation (14)	$(M/\theta) = a + b * \Sigma \Delta \theta_i + c (\Sigma \Delta \theta_i)^m$
Equation (15)	$(T_b/\theta) = a + b * \Sigma \Delta \theta_i + c (\Sigma \Delta \theta_i)^m$
Equation (16)	$\theta = a + b * \Sigma \Delta \theta_i + c (\Sigma \Delta \theta_i)^m + d (\Sigma \Delta \theta_i)^n$
Equation (17)	$\exp(\theta/p) = a + b * \Sigma \Delta \theta_i + c (\Sigma \Delta \theta_i)^m + d (\Sigma \Delta \theta_i)^n$
Equation (18)	$(1/\theta)^p = a + b * \Sigma \Delta \theta_i + c (\Sigma \Delta \theta_i)^m + d (\Sigma \Delta \theta_i)^n$
Equation (19)	$(M/\theta) = a + b * \Sigma \Delta \theta_i + c (\Sigma \Delta \theta_i)^m + d (\Sigma \Delta \theta_i)^n$
Equation (20)	$(T_b/\theta) = a + b * \Sigma \Delta \theta_i + c (\Sigma \Delta \theta_i)^m + d (\Sigma \Delta \theta_i)^n$

The nonlinear regression of the data was conducted using the Levenberg-Marquardt algorithm for each property. In order to test the reliability of the different equations, we determine for each one the average absolute deviations AAD (%) registered in the case of each hydrocarbon family.

The results obtained are summarised in Tables 2, 3 and 4 respectively for boiling point, freezing point and density. The number of data used for each regression, and their distribution in terms of carbon atom numbers are also given in these tables.

In selecting the best equation that best fitted the data, we compare between the deviations registered by the different equations tested taking into account all the families. Also, we compare their ability in extrapolating the data to heavier compounds.

### 1.1 Selecting Equation for Estimating Boiling Point

For boiling point, we registered the higher deviations for the first terms of each family, particularly for ones that are in the gaseous state at ambient temperature. Equations for which we didn't give any results, have been eliminated because

they provided some very important gaps in relation to reference data.

The results given in Table 2 show that Equations (11, 14, 16, 17 and 19) give the smallest average deviations. In a first approach, we select them as the best equations for the evaluation of the boiling point of pure hydrocarbons. In a second stage, we compare their ability to predict this property for hydrocarbons with high carbon numbers. For this purpose, we take like reference the Riazi and El Sahhaf (1995) Equation that joins the boiling points of normal-paraffins to their carbon atom numbers. Indeed, the application of this correlation to heavy compounds has been largely proved. On this basis, we select Equation (11) as the best correlation that satisfies the two criteria of selection.

## 1.2 Selecting Equation for Estimating Freezing Point

In the case of the freezing point, like shown in Table 3, the deviations obtained comparatively to the reference data remain high enough for most hydrocarbons, with the exception of normal paraffins. In spite of this, we kept equations that provided the relatively weakest errors. So, we selected Equations (4, 5, 9, 14 and 16) in a first step. Thereafter, and while comparing their faculty to estimate correctly freezing points of heavy *n*-paraffins while taking in

reference the correlation of Riazi and El Sahhaf (1995), we keep the Equation (14) as the group-contribution correlation which predict best this property.

## 1.3 Selecting Equation for Estimating Liquid Density

For the density, results given in Table 4 show that the registered deviations are in general satisfactory, with the exception of the aromatics that sometimes give some elevated errors, especially for the first terms of this hydrocarbon family. While comparing the average deviations registered on the set of hydrocarbons, Equations (2, 4, 7, 9, 14, 15, 19 and 20) are selected as those that provided the best results. As far as the second criteria of selection is concerned, we take as reference the value of 856 kg/m<sup>3</sup> given by Wuithier (1972) as the limiting value toward which tend the liquid density of long chain hydrocarbons. As a result, Equation (9) is kept for the prediction of this property.

## 1.4 Equations Parameters

The values of the group-contribution parameters and those of the constants *a*, *b*, *c*, *d*, *m*, *n* and *p* of the selected equations are given in Table 5.

TABLE 2  
Comparison between the AAD of the different equations predicting boiling point

	<i>n</i> -paraffins	<i>i</i> -paraffins	Olefins	Alcyns	Naphthenes	Aromatics	AAD (%)
Data points	79	761	293	87	327	256	1803
Carbon range	C <sub>2</sub> -C <sub>80</sub>	C <sub>4</sub> -C <sub>100</sub>	C <sub>2</sub> -C <sub>100</sub>	C <sub>2</sub> -C <sub>40</sub>	C <sub>3</sub> -C <sub>102</sub>	C <sub>6</sub> -C <sub>102</sub>	
Eq. (1)	–	–	–	–	–	–	–
Eq. (2)	1.10	0.97	1.36	1.73	1.60	1.52	1.27
Eq. (3)	2.83	1.24	2.93	3.09	4.77	2.73	2.53
Eq. (4)	–	–	–	–	–	–	–
Eq. (6)	–	–	–	–	–	–	–
Eq. (7)	1.10	0.97	1.36	1.73	1.60	1.52	1.27
Eq. (8)	2.83	1.24	2.92	3.09	4.75	2.74	2.52
Eq. (9)	2.02	1.17	2.35	4.24	2.07	1.77	1.80
Eq. (11)	0.11	0.78	0.61	0.39	0.99	0.95	0.77
Eq. (12)	0.64	0.99	1.01	1.44	1.15	1.11	1.05
Eq. (13)	2.83	1.24	2.93	3.09	4.75	2.73	2.52
Eq. (14)	0.15	0.74	0.74	0.42	0.96	0.88	0.76
Eq. (16)	0.12	0.78	0.61	0.39	1.00	0.89	0.76
Eq. (17)	0.37	0.88	0.72	1.20	1.04	0.96	0.89
Eq. (18)	2.83	1.24	2.92	3.09	8.69	2.74	3.24
Eq. (19)	0.15	0.74	0.72	0.42	0.91	0.87	0.74

\* Equations (5, 10, 15 and 20) are not considered for the boiling point.

TABLE 3

Comparison between the AAD of the different equations predicting freezing point

	<i>n</i> -paraffins	<i>i</i> -paraffins	Olefins	Alcyns	Naphthenes	Aromatics	AAD (%)
Data points	39	88	121	54	153	122	577
Carbon range	C <sub>2</sub> -C <sub>40</sub>	C <sub>4</sub> -C <sub>20</sub>	C <sub>2</sub> -C <sub>40</sub>	C <sub>2</sub> -C <sub>40</sub>	C <sub>3</sub> -C <sub>42</sub>	C <sub>6</sub> -C <sub>42</sub>	-
Eq. (1)	-	-	-	-	-	-	-
Eq. (2)	4.20	9.81	10.65	8.12	11.11	8.76	9.57
Eq. (3)	-	-	-	-	-	-	-
Eq. (4)	2.81	9.32	8.35	8.08	9.18	9.17	8.49
Eq. (5)	3.51	10.51	9.31	6.09	9.43	9.76	8.93
Eq. (6)	-	-	-	-	-	-	-
Eq. (7)	4.20	9.81	10.64	8.12	11.09	8.76	9.56
Eq. (8)	-	-	-	-	-	-	-
Eq. (9)	2.81	9.32	8.35	8.09	4.30	9.17	7.20
Eq. (10)	3.51	10.51	9.31	6.10	9.44	9.77	8.93
Eq. (11)	2.42	9.71	9.47	8.09	9.98	9.15	8.97
Eq. (12)	2.33	9.8	9.64	8.21	10.01	9.16	9.03
Eq. (13)	5.78	9.50	11.81	8.17	12.67	8.55	10.25
Eq. (14)	1.94	9.37	8.25	8.34	9.40	8.87	8.44
Eq. (15)	2.03	10.78	11.21	7.45	13.74	10.80	10.76
Eq. (16)	2.38	9.74	9.50	8.13	9.96	9.15	8.98
Eq. (17)	1.16	12.11	10.79	7.81	12.19	9.27	10.11
Eq. (18)	2.33	9.78	9.55	8.21	13.92	9.19	10.05
Eq. (19)	1.94	9.37	8.29	8.31	9.49	12.16	9.16
Eq. (20)	1.78	10.23	9.98	7.74	11.41	10.63	9.77

TABLE 4

Comparison between the AAD of the different equations predicting liquid density at 20°C

	<i>n</i> -paraffins	<i>i</i> -paraffins	Olefins	Alcyns	Naphthenes	Aromatics	AAD (%)
Data points	35	677	227	85	264	197	1485
Carbon range	C <sub>5</sub> -C <sub>40</sub>	C <sub>5</sub> -C <sub>20</sub>	C <sub>4</sub> -C <sub>40</sub>	C <sub>4</sub> -C <sub>40</sub>	C <sub>4</sub> -C <sub>42</sub>	C <sub>6</sub> -C <sub>40</sub>	-
Eq. (1)	2.37	1.21	2.23	2.41	3.09	3.39	2.09
Eq. (2)	0.46	1.11	1.30	1.66	1.95	3.11	1.57
Eq. (3)	-	-	-	-	-	-	-
Eq. (4)	0.19	0.89	0.93	0.92	2.76	1.57	1.30
Eq. (5)	-	-	-	-	-	-	-
Eq. (6)	2.37	1.21	2.23	2.41	3.09	3.55	2.11
Eq. (7)	0.46	1.11	1.30	1.66	1.95	3.12	1.57
Eq. (8)	-	-	-	-	-	-	-
Eq. (9)	0.19	0.89	0.93	0.92	2.76	1.57	1.30
Eq. (10)	-	-	-	-	-	-	-
Eq. (11)	0.15	1.03	1.15	1.51	2.54	9.11	2.40
Eq. (12)	0.10	1.04	1.15	1.47	2.44	8.73	2.33
Eq. (13)	0.15	1.03	1.15	1.51	2.53	9.32	2.42
Eq. (14)	0.09	0.89	0.91	0.94	2.67	1.57	1.28
Eq. (15)	0.09	0.56	0.61	0.69	1.97	1.11	0.89
Eq. (16)	0.13	1.04	1.15	1.51	2.01	9.25	2.32
Eq. (17)	0.08	1.04	1.15	1.50	2.50	8.60	2.32
Eq. (18)	0.12	1.04	1.15	1.50	2.48	8.88	2.36
Eq. (19)	0.06	0.90	0.94	0.98	2.17	1.59	1.21
Eq. (20)	0.10	0.56	0.62	0.70	1.97	1.11	0.89

TABLE 5  
Parameters values and group increments values of Equation F

Equation	$T_b$	$T_f$	$d_{20}$
	Eq. (11)	Eq. (14)	Eq. (9)
<b>Parameter values</b>			
$p$	—	—	—
$a$	2.10497E+03	-5.32928E-01	-3.91046E-01
$b$	-1.77440E-01	3.05306E-01	3.49011E-01
$c$	-6.19434E+03	6.06110E-01	—
$d$	—	—	—
$m$	-2.80170E-01	-4.38977E-01	—
$n$	—	—	—
<b>Contributions</b>			
- CH <sub>3</sub>	3.36103E+01	6.80429E-01	6.53292E-01
- CH <sub>2</sub>	6.01945	1.23893E-01	4.67606E-02
- CH<	-2.28076E+01	-4.92776E-01	-5.76890E-01
>C<	-5.10314E+01	-1.30057	-1.20711
= CH <sub>2</sub>	3.29791E+01	6.61299E-01	6.52976E-01
= CH-	6.33765	2.93538E-01	3.46579E-02
= C<	-2.11492E+01	-6.60729E-01	-5.89958E-01
= C=	7.94780	-2.35470E-01	2.10506E-02
≡ CH	3.27471E+01	6.15015E-01	6.39500E-01
≡ C-	7.19358	9.32368E-02	2.28269E-02
<b>Corrections terms owed to the CH<sub>3</sub> proximity effects</b>			
C(CH <sub>3</sub> ) <sub>3</sub>	-1.73388	3.87264E-01	4.01010E-02
C(CH <sub>3</sub> ) <sub>2</sub>	-9.13930E-01	3.57568E-01	1.99574E-02
C(CH <sub>3</sub> )	-5.50980E-01	2.64643E-01	4.70667E-03
C(CH <sub>3</sub> )C(CH <sub>3</sub> )	7.10180E-01	-1.52738E-01	2.08435E-03
C(CH <sub>3</sub> )C(CH <sub>3</sub> ) <sub>2</sub>	1.21475	7.38494E-02	1.44740E-04
C(CH <sub>3</sub> )C(CH <sub>3</sub> ) <sub>3</sub>	1.82757	2.48059E-03	-5.22518E-03
C(CH <sub>3</sub> ) <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub>	2.12237	9.90933E-02	-4.61323E-03
C(CH <sub>3</sub> ) <sub>2</sub> C(CH <sub>3</sub> ) <sub>3</sub>	3.45589	-6.34782E-01	-1.03234E-02
<b>Corrections terms owed to the types of positions</b>			
<i>cis</i> -	-1.42400E-01	7.82603E-02	2.37399E-03
<i>trans</i> -	-2.01200E-01	-6.96987E-02	4.04111E-03
<b>Corrections terms owed to the ring structure</b>			
3 membered ring	5.67167E+01	-6.70642E-02	1.21925
4 membered ring	5.67215E+01	1.14841	1.19909
5 membered ring	5.67392E+01	1.63831	1.20410
6 membered ring	5.79497E+01	1.31182	1.18562
7 membered ring	5.99484E+01	5.96939E-02	1.14001
8 membered ring	6.15173E+01	1.75399E-01	1.13091
9 membered ring	6.24661E+01	4.60262E-01	1.12504
10 membered ring	6.29563E+01	6.05954E-01	1.12153
11 membered ring	6.25620E+01	1.04145	1.11894
12 membered ring	6.21962E+01	4.11652E-01	1.11816
13 membered ring	6.18293E+01	7.85851E-01	1.11867
14 membered ring	6.10686E+01	5.98616E-01	1.11929
15 membered ring	6.05805E+01	5.91201E-01	1.12084
16 membered ring	5.99864E+01	6.59633E-01	1.12262
17 membered ring	5.92470E+01	6.81649E-01	1.12462
18 membered ring	5.83214E+01	6.68171E-01	1.12685
19 membered ring	5.76199E+01	—	1.12931
20 membered ring	5.66837E+01	—	1.13200
<b>Corrections terms owed to the aromatic structures</b>			
Aromatic ring	5.61560E+01	4.97120E-01	1.20018
Ortho-substitution	2.87670E-01	4.03396E-01	5.95223E-03
Meta-substitution	7.10900E-02	5.57575E-01	1.15111E-02
Para-substitution	7.10900E-02	5.57575E-01	1.15111E-02
Substitution in positions 1-2-3	1.29240	5.74670E-01	1.24819E-02
Substitution in positions 1-2-4	9.73490E-01	7.93313E-01	2.10110E-02
Substitution in positions 1-3-5	-6.73900E-01	9.72197E-01	2.43517E-02
Substitution in positions 1-2-5	1.30243	4.36259E-01	1.33045E-02
Substitution in positions 1-2-6	1.14308	4.47632E-01	1.13885E-02
Substitution in positions 1-3-4	-3.53680E-01	9.50403E-01	1.95087E-02
Substitution in positions 1-2-4-5	2.40917	4.63746E-01	3.13636E-02
Substitution in positions 1-2-3-4	4.09709	7.29045E-01	2.31769E-02
Substitution in positions 1-2-3-5	2.32485	9.25268E-01	2.99362E-02
Substitution in positions 1-2-3-4-5	7.39249	7.34520E-01	3.21448E-02

## 2 METHOD ACCURACY

In order to test the accuracy of the proposed equations, we have compared their average absolute deviations to those registered by other methods given in literature and using the chemical structure to predict the studied properties. The results obtained and given in Table 6 show that our method give in each case the best results with regard to reference data, notably in the case of the boiling point.

## 3 EXAMPLES

To illustrate the proposed method, we provide in Tables 7 to 14 the estimation of the boiling point, freezing point and liquid density of *n*-hexadecane (*n*-paraffin), 2,3,3-trimethylpentane (iso-paraffin), 2-methyl-1-nonene (olefin), 1-dodecyn (alcyn), 1-ethyl-*cis*-2-methylcyclopentane (naphthene), 1,1-dicyclohexyl-dodecane (naphthene), 1,4-isopropyltoluene (aromatic) and 2,4'-dimethyldiphenylmethane (aromatic).

TABLE 6

Comparison of the accuracy between existing correlations and the proposed equations

	<i>n</i> -paraffins	<i>i</i> -paraffins	Olefins	Alcyns	Naphthenes	Aromatics
<b>Boiling point</b>						
	<b>AAD (%)</b>					
Proposed method	<b>0.11</b>	<b>0.78</b>	<b>0.61</b>	<b>0.39</b>	<b>0.99</b>	<b>0.95</b>
Joback (1984)	48.79	9.62	2.29	7.70	24.22	29.48
Constantinou (1994)	6.28	1.89	3.27	3.98	3.59	3.42
Kreglewski-Zwolinsky (1961)	0.22	–	–	–	–	–
Riazi and El Sahhaf (1995)	0.22	–	–	–	–	–
<b>Freezing point</b>						
	<b>AAD (%)</b>					
Proposed method	<b>1.94</b>	<b>9.37</b>	<b>8.25</b>	<b>8.34</b>	9.40	8.87
Joback (1984)	19.67	10.38	12.84	31.47	22.06	20.62
Constantinou (1994)	8.34	14.96	7.48	14.50	11.45	9.01
Riazi and El Sahhaf (1995)	2.77	–	–	–	–	–

TABLE 7

Estimation of the boiling point, freezing point and liquid density of *n*-hexadecane

Groups	$T_b$	$T_F$	$d_{20}$
2 -CH <sub>3</sub>	2 x 33.6103	2 x 0.680429	2 x 0.653292
14 -CH <sub>2</sub> -	14 x 6.01945	14 x 0.123893	14 x 0.0467606
Calculated value	560.6 K	289.9 K	771.7 kg/m <sup>3</sup>
Experimental value	560.0 K	291.3 K	773.5 kg/m <sup>3</sup>
Absolute deviation (%)	0.1	0.5	0.2

TABLE 8

Estimation of the boiling point, freezing point and liquid density of 2,3,3-trimethylpentane

Groups	$T_b$	$T_F$	$d_{20}$
5 -CH <sub>3</sub>	5 x 33.6103	5 x 0.680429	5 x 0.653292
1 -CH <sub>2</sub> -	1 x 6.01945	1 x 0.123893	1 x 0.0467606
1 >CH-	1 x (-22.8076)	1 x (-0.492776)	1 x (-0.57689)
1 >C<	1 x (-51.0314)	1 x (-1.30057)	1 x (-1.20711)
<b>Correction terms</b>			
2 C(CH <sub>3</sub> ) <sub>2</sub>	2 x (-0.91393)	2 x 0.357568	2 x 0.0199574
1 C(CH <sub>3</sub> )	1 x (-0.55098)	1 x 0.264643	1 x 0.00470667
1 C(CH <sub>3</sub> )C(CH <sub>3</sub> ) <sub>2</sub>	1 x 1.21475	1 x 0.0738494	1 x 1.4470E-04
1 C(CH <sub>3</sub> ) <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub>	1 x 2.12237	1 x 0.0990933	1 x (-0.00461323)
Calculated value	387.9 K	156.8 K	729.1 kg/m <sup>3</sup>
Experimental value	387.9 K	172.5 K	726.2 kg/m <sup>3</sup>
Absolute deviation (%)	0.0	9.1	0.4

TABLE 9

Estimation of the boiling point, freezing point and liquid density of 2-methyl-1-nonene

Groups	$T_b$	$T_F$	$d_{20}$
2 CH <sub>3</sub>	2 x 33.6103	2 x 0.680429	2 x 0.653292
6 -CH <sub>2</sub> -	6 x 6.01945	6 x 0.123893	6 x 0.0467606
1 = CH <sub>2</sub>	1 x 32.9791	1 x 0.661299	1 x 0.652976
1 = C<	1 x (-21.1492)	1 x (-0.660729)	1 x (-0.589958)
<b>Correction terms</b>			
2 C(CH <sub>3</sub> )	2 x (-0.55098)	2 x 0.264643	2 x 0.00470667
Calculated value	441.7 K	210.2 K	745.5 kg/m <sup>3</sup>
Experimental value	441.5 K	208.9 K	745.1 kg/m <sup>3</sup>
Absolute deviation (%)	0.05	0.6	0.05

TABLE 10

Estimation of the boiling point, freezing point and liquid density of 1-dodecyne

Groups	$T_b$	$T_F$	$d_{20}$
1 CH <sub>3</sub>	1 x 33.6103	1 x 0.680429	1 x 0.653292
9-CH <sub>2</sub> -	9 x 6.01945	9 x 0.123893	9 x 0.0467606
1 ≡ C-	1 x 7.19358	1 x 0.0932368	1 x 0.0228269
1 ≡ CH	1 x 32.7471	1 x 0.615015	1 x 0.6395
Calculated value	490.5 K	261.2 K	773.5 kg/m <sup>3</sup>
Experimental value	488.0 K	254.2 K	780.9 kg/m <sup>3</sup>
Absolute deviation (%)	0.5	2.8	0.9

TABLE 11

Estimation of the boiling point, freezing point and liquid density of 1-ethyl-*cis*-2-methylcyclopentane

Groups	$T_b$	$T_F$	$d_{20}$
2-CH <sub>3</sub>	2 x 33.6103	2 x 0.680429	2 x 0.653292
4-CH <sub>2</sub> -	4 x 6.01945	4 x 0.123893	4 x 0.0467606
2-CH<	2 x (-22.8076)	2 x (-0.492776)	2 x (-0.57689)
<b>Correction terms</b>			
Position <i>cis</i> - 5 membered ring	-0.1424 56.7392	0.0782603 1.63831	0.00237399 1.2041
Calculated value	392.8 K	171.0 K	755.0 kg/m <sup>3</sup>
Experimental value	401.2 K	167.2 K	785.2 kg/m <sup>3</sup>
Absolute deviation (%)	2.1	2.3	3.9

TABLE 12

Estimation of the boiling point, freezing point and liquid density of 1,1-dicyclohexyl-dodecane

Groups	$T_b$	$T_F$	$d_{20}$
1 -CH <sub>3</sub>	1 x 33.6103	1 x 0.680429	1 x 0.653292
20 -CH <sub>2</sub> -	20 x 6.01945	20 x 0.123893	20 x 0.0467606
3 >CH-	3 x (-22.8076)	3 x (-0.492776)	3 x (-0.57689)
<b>Correction terms</b>			
2 (6 membered ring)	2 x 57.9497	2 x 1.31182	2 x 1.18562
Calculated value	668.3 K	304.1 K	864.8 kg/m <sup>3</sup>
Experimental value	660.0 K	-	875.4 kg/m <sup>3</sup>
Absolute deviation (%)	1.3	-	1.2

TABLE 13

Estimation of the boiling point, freezing point and liquid density of 1,4-isopropyltoluene

Groups	$T_b$	$T_F$	$d_{20}$
3 CH <sub>3</sub>	3 x 33.6103	3 x 0.680429	3 x 0.653292
1 > CH-	1 x (-22.8076)	1 x (-0.492776)	1 x (-0.57689)
4 = CH-	4 x 6.33765	4 x 0.293538	4 x 0.0346579
2 = C<	2 x (-21.1492)	2 x (-0.660729)	2 x (-0.589958)
<b>Correction terms</b>			
1 (aromatic ring)	1 x 56.156	1 x 0.49712	1 x 1.20018
1 (substitution para-)	1 x 0.85273	1 x 0.24589	1 x 0.0124819
Calculated value	456.9 K	241.7 K	886.3 kg/m <sup>3</sup>
Experimental value	450.3 K	205.2 K	857.3 kg/m <sup>3</sup>
Absolute deviation (%)	1.5	17.8	3.4

TABLE 14

Estimation of the boiling point, freezing point and liquid density of 2,4'-dimethyldiphenylmethane

Groups	$T_b$	$T_F$	$d_{20}$
2 CH <sub>3</sub>	2 x 33.6103	2 x 0.680429	2 x 0.653292
1 CH <sub>2</sub>	1 x 6.01945	1 x 0.123893	1 x 0.0467606
8 = CH-	8 x 6.33765	8 x 0.293538	8 x 0.0346579
4 = C<	4 x (-21.1492)	4 x (-0.660729)	4 x (-0.589958)
<b>Correction terms</b>			
2 (aromatic ring)	2 x 56.156	2 x 0.49712	2 x 1.20018
1 (substitution ortho-)	1 x 0.28767	1 x 0.403396	1 x 0.00595223
1 (substitution para-)	1 x 0.85273	1 x 0.24589	1 x 0.0124819
Calculated value	564.0 K	274.2 K	989.0 kg/m <sup>3</sup>
Experimental value	571.0 K	-	988.0 kg/m <sup>3</sup>
Absolute deviation (%)	1.2	-	0.1

## CONCLUSION

A new group-contribution method is developed to predict boiling point, freezing point and liquid density at 20°C of pure hydrocarbons. A number of structural groups were derived from the data bank, a particular care was taken in detecting differences between molecules, particularly in the case of isomers.

The results show that the proposed model for each property lead to good correlation with experimental data and give better deviations comparatively to other correlations recommended in literature. Besides, the proposed equations remain valid in the case of the heavy hydrocarbons, what is not the case of the other methods.

An extension of the present work will consist in the future in the study of other physical and thermodynamic properties such as critical and thermal properties with the same approach and the application of the established correlations to petroleum fractions.

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