PREDICTION OF PHYSICAL PROPERTIES OF HYDROCARBONS AND PETROLEUM FRACTIONS BY A NEW GROUP- CONTRIBUTION METHOD

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Abstract. *A new group contribution method for the estimation of critical temperature, critical pressure, critical volume, enthalpy of vaporization at the normal boiling point, refractive index parameter and molar volume at 20°C is developed. The results show good consistency among various properties and give better deviations comparatively to other correlations recommended in literature. These new equations were also used to estimate the properties of petroleum fractions. For this purpose, a new characterization method is proposed. The comparison between predicted properties and that calculated by other correlations given in literature, yields a very satisfactory results.*

Key words: *correlations, group- contributions, physical properties, hydrocarbons, petroleum fractions.*

Introduction

The knowledge of physical properties of hydrocarbons and petroleum fractions is primordial in the design of most processes for both production and refining of crude oils. Many correlations have been proposed in literature to estimate these parameters. Methods based only on the molecular structure of a compound, called group- contribution methods, are widely used. 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 proposed a group- contribution method to estimate critical temperature (K), critical pressure (bar), critical volume (cm³/mol), enthalpy of vaporization at normal boiling point (kj/mol), refractive index parameter and molar volume at 20°C (cm³/mol) of pure hydrocarbons. The established equations were used to estimate the physical properties of petroleum fractions. For this purpose, a characterization method of petroleum products is proposed to simulate a fraction by a simple mixture. Then, additivity rules are used to evaluate the average properties of these products.

Proposed Method

To carry out this study, we first proceed to the compilation of properties values of pure hydrocarbons from the TRC data base (TRC, Thermodynamic Data Base, version 1.3, 1994) [1]. A set of more than 1300 hydrocarbons belonging to n-paraffins, iso- paraffins, olefins, alcyns, naphthenes and aromatics groups was used for the calculation of model parameters. The second step consists in selecting the atomic groups to be used. The experience of previous workers was very helpful. We selected 10 types of groups: CH_3, CH_2, CH, C, $=CH_2$, $=CH$, $=C$, $=C=$, $\equiv CH$ and $\equiv C$, without any distinction between a carbon atom appearing in a ring and a nonring structures. After, we included correction terms to take into account some specific structures. Thus, terms were affected to allow proximity effects of CH_3 groups in hydrocarbons which belong to the isoparaffin. Terms were assigned to ring correction to correct for possible stress-strain effects in such molecules. Cis and trans contribution are also included to take care of isomerization in naphthene and alkene compounds. For aromatic structures, a ring correction was added in addition to those relative to ortho, meta and para substitutions and other substitution types.

The generation of the group additivity parameters was followed by the data analysis to develop a group additivity relationship. We tried several equations which can be generalized in mathematical form by the following relationship:

$$F(\theta)= a.+ b. \ \Sigma\Delta\theta_i + c. \ (\Sigma\Delta\theta_i)^m + d. \ (\Sigma\Delta\theta_i)^n \qquad (1)$$

Where θ is a given property and $F(\theta)$ a function equal to θ, $\exp(\theta/p)$, $1/\theta^p$, M/θ or Tb/θ. a, b, c, d, m, n and p are constants determined by regression. T_b (K) and M(g/mol) are respectively the boiling point and the molecular weight. Twenty equations are derived from the generalized equation as shown in table 1.

The aim of this approach is to test different forms of mathematical equations to provide the best correlation with a minimum error.

Table 1. The different forms of equation F(θ)

$$\theta = b*\Sigma\Delta\theta_I \tag{1-1}$$
$$Exp(\theta/p) = b*\Sigma\Delta\theta_I \tag{1-2}$$
$$(1/\theta)^p = b*\Sigma\Delta\theta_I \tag{1-3}$$
$$(M/\theta) = b*\Sigma\Delta\theta_I \tag{1-4}$$
$$(Tb/\theta) = b*\Sigma\Delta\theta_I \tag{1-5}$$
$$\theta = a.+b*\Sigma\Delta\theta_I \tag{1-6}$$
$$Exp(\theta/p) = a.+b*\Sigma\Delta\theta_i \tag{1-7}$$
$$(1/\theta)^p = a.+b*\Sigma\Delta\theta_I \tag{1-8}$$
$$(M/\theta) = a.+b*\Sigma\Delta\theta_I \tag{1-9}$$
$$(Tb/\theta) = a.+b*\Sigma\Delta\theta_I \tag{1-10}$$
$$\theta = a.+b*\Sigma\Delta\theta_i + c\,(\Sigma\Delta\theta_i)^m \tag{1-11}$$
$$Exp(\theta/p) = a.+b*\Sigma\Delta\theta_i + c\,(\Sigma\Delta\theta_i)^m \tag{1-12}$$
$$(1/\theta)^p = a.+b*\Sigma\Delta\theta_i + c\,(\Sigma\Delta\theta_i)^m \tag{1-13}$$
$$(M/\theta) = a.+b*\Sigma\Delta\theta_i + c\,(\Sigma\Delta\theta_i)^m \tag{1-14}$$
$$(Tb/\theta) = a.+b*\Sigma\Delta\theta_i + c\,(\Sigma\Delta\theta_i)^m \tag{1-15}$$
$$\theta = a.+b*\Sigma\Delta\theta_i + c\,(\Sigma\Delta\theta_i)^m + d\,(\Sigma\Delta\theta_i)^n \tag{1-16}$$
$$Exp(\theta/p) = a.+b*\Sigma\Delta\theta_i + c\,(\Sigma\Delta\theta_i)^m + d\,(\Sigma\Delta\theta_i)^n \tag{1-17}$$
$$(1/\theta)^p = a.+b*\Sigma\Delta\theta_i + c\,(\Sigma\Delta\theta_i)^m + d\,(\Sigma\Delta\theta_i)^n \tag{1-18}$$
$$(M/\theta) = a.+b*\Sigma\Delta\theta_i + c\,(\Sigma\Delta\theta_i)^m + d\,(\Sigma\Delta\theta_i)^n \tag{1-19}$$
$$(Tb/\theta) = a.+b*\Sigma\Delta\theta_i + c\,(\Sigma\Delta\theta_i)^m + d\,(\Sigma\Delta\theta_i)^n \tag{1-20}$$

For each property, the nonlinear regression of the data was conducted using the Levenberg- Marquardt algorithm.

Results and Discussion

In order to test the reliability of the different equations, we determine for each property the average absolute deviations AAD (%) registered in the case of each hydrocarbon group. 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 long chain hydrocarbons. The results obtained are summarized in table 2.

The parameter values of the established equations and the group- contribution parameters are reported in table 3.

Method Accuracy

To test the accuracy of the proposed equations, we have compared their average absolute deviations to those registered by other methods recommended in literature. The obtained results are given in table 4 and show that our approach gives for most properties significantly more accurate predictions, particularly for branched paraffins.

Table 2. Average deviations registered for the selected equations

Property	Eq.	n-paraffins	i-paraffins	olefins	alcyns	naphthenes	aromatics	AAD (%)
T_C	1-15	0.2	0.3	0.3	0.8	0.4	0.4	0.4
P_C	1-13	7.2	0.5	3.7	7.1	11.3	6.5	4.5
V_C	1-1	1.6	0.9	1.7	2.6	1.8	3.0	1.7
Hv	1-15	0.3	0.8	1.2	-	0.9	1.7	1.0
I	1-18	0.01	1.0	1.4	1.1	1.8	2.1	1.5
V_M	1-6	1.0	0.9	1.0	0.8	2.7	1.6	1.4

Table 3. Equations' parameters

	T_C	P_C	V_C	Hv	I	V_M
Equations parameters						
p	-	3.76621E-01	-	-	9,97817E+00	-
a	3.75032E-02	2.32562E-01	-	3,98140E+00	3,63704E+05	-1,68509E+01
b	-3.52119E-03	3.05702E-02	5.32007E+00	-1,04126E-01	-1,34807E+03	8,94240E-01
c	6.74016E-01	6.20589E-02	-	7,87237E+00	4,47270E+06	-
d	-	-	-	-	-1,19750E+03	-
m	1.91890E-01	8.29137E-01	-	-1,20399E-01	-1,36506E+00	-
n	-	-	-	-	-1,65795E+01	-
Contributions						
-CH$_3$	1.99670E-01	1.98848E-05	1.31664E+01	2,40567E-01	-1,73990E-01	4,41078E+01
-CH$_2$-	9.15532E-02	1.12008E-01	1.06879E+01	1,19053E-01	5,23300E-01	1,83338E+01
-CH<	-6.11156E-02	2.01649E-01	5.15453E+00	6,02534E-02	2,12424E+00	-1,40334E+01
>C<	-2.48688E-01	2.45728E-01	-9.39285E-01	-5,53860E-02	3,91591E+00	-4,89585E+01
=CH$_2$	1.89248E-01	1.11136E-02	1.18505E+01	1,63323E-01	-1,64130E-01	4,48161E+01
=CH-	7.10096E-02	5.37104E-02	8.20223E+00	1,18567E-01	1,19727E+00	1,42536E+01
=C<	-5.34718E-02	1.15424E-01	4.70117E+00	1,59184E-01	3,08689E+00	-1,87630E+01
=C=	4.92851E-02	-2.22262E-02	9.52029E+00	-	2,85119E+00	9,58008E+00
≡CH	2.02609E-01	3.96981E-07	9.02010E+00	-	-5,77680E-01	3,80555E+01
≡C-	6.07703E-02	3.42040E-02	6.68835E+00	-	1,66997E+00	1,06352E+01

Corrections terms due to the CH3 proximity effects						
$C(CH_3)_3$	3.53048E-02	3.73376E-02	4.22093E+00	-2,85760E-01	-1,61553E+00	1,66121E+01
$C(CH_3)_2$	7.25627E-03	8.81017E-03	1.82988E+00	-1,91433E-01	-9,42120E-01	8,54753E+00
$C(CH_3)$	-6.78177E-03	-1.62746E-02	-1.02605E-01	-8,88038E-02	-2,88570E-01	2,41638E+00
$C(CH_3)C(CH_3)$	1.72578E-03	6.44537E-04	5.58189E-01	-3,01832E-03	-4,18300E-02	6,32070E-01
$C(CH_3)C(CH_3)_2$	6.58727E-03	-9.25088E-03	3.74734E-01	-8,65325E-03	1,30250E-01	-1,91800E-01
$C(CH_3)C(CH_3)_3$	-1.37746E-02	-1.15443E-02	-4.72746E-01	-5,21660E-02	-2,12830E-01	-2,43714E+00
$C(CH_3)_2C(CH_3)_2$	-1.13700E-02	-4.75291E-02	-6.13219E-01	-3,49965E-02	3,32230E-01	-2,04880E+00
$C(CH_3)_2C(CH_3)_3$	-2.57257E-02	-5.68499E-02	-1.08514E+00	4,51564E-02	4,75600E-02	-3,78122E+00
Corrections terms due to the types of positions						
cis	7.68223E-03	2.14235E-02	1.54374E+00	4,16289E-02	3,68300E-02	1,36244E+00
trans	2.00218E-02	5.62534E-02	1.67532E+00	5,21288E-02	-8,02700E-02	1,99634E+00
Corrections terms due to the ring structure						
3 membered ring	1.33081E-01	-3.36020E-01	-1.46258E+00	4,18875E-01	-2,38277E+00	5,61678E+01
4 membered ring	1.12379E-01	-3.63950E-01	-3.09044E+00	4,74070E-01	-1,12037E+00	4,89982E+01
5 membered ring	1.12121E-01	-2.91276E-01	-3.10119E+00	-8,28247E-02	-6,07980E-01	4,80489E+01
6 membered ring	7.88993E-02	-3.04600E-01	-4.96039E+00	-2,91990E-01	2,77938E+00	4,06182E+01
7 membered ring	-2.96855E-02	-4.40665E-01	-7.33493E+00	1,08317E-01	6,24363E+00	2,58967E+01
8 membered ring	-8.32130E-02	-4.69314E-01	-8.81242E+00	-1,64740E-02	1,46886E+01	2,22592E+01
9 membered ring	-1.38309E-01	-4.88434E-01	-1.02899E+01	-1,35588E-01	2,65938E+01	1,98859E+01
10 membered ring	-1.82415E-01	-4.85558E-01	-1.17674E+01	-2,51568E-01	3,84727E+01	1,84310E+01
11 membered ring	-	-	-	-	5,09464E+01	1,73393E+01
12 membered ring	-	-	-	-	5,35118E+01	1,69495E+01
13 membered ring	-	-	-	-	5,29898E+01	1,70658E+01
14 membered ring	-	-	-	-	4,93806E+01	1,72249E+01
15 membered ring	-	-	-	-	4,58045E+01	1,77455E+01
16 membered ring	-	-	-	-	3,93303E+01	1,83541E+01
17 membered ring	-	-	-	-	3,59399E+01	1,90514E+01
18 membered ring	-	-	-	-	3,26425E+01	1,98379E+01
19 membered ring	-	-	-	-	2,94533E+01	2,07142E+01
20 membered ring	-	-	-	-	2,39764E+01	2,16811E+01
Corrections terms due to the aromatic structures						
Aromatic ring	1.09046E-01	-2.45525E-01	4.44276E+00	-1,72772E-01	9,15520E+01	4,45403E+01
Ortho substitution	-3.65254E-03	2.57744E-02	-4.08265E+00	-1,53867E-02	1,50047E+01	2,54983E+00
Meta substitution	6.98374E-03	4.87704E-02	-3.86336E+00	-3,90781E-04	1,19657E+01	4,90251E+00
Para substitution	1.10481E-02	5.96276E-02	-3.70672E+00	-7,30870E-02	1,36120E+01	5,44357E+00
Substitution in positions 1-2-3	2.28164E-02	6.55366E-02	-2.56483E+00	-3,06678E-03	2,65694E+01	7,17371E+00
Substitution in positions 1-2-4	4.09258E-02	1.14323E-01	-2.62311E+00	-1,32382E-01	2,01392E+01	8,88411E+00
Substitution in positions 1-3-5	6.20632E-02	1.30913E-01	-2.56483E+00	-2,09531E-02	1,53820E+01	1,11715E+01
Substitution in positions 1-2-5	-	-	-	-	6,33411E+01	5,92909E+00
Substitution in positions 1-2-6	3.68598E-02	1.26470E-01	-2.73968E+00	-2,58889E-01	2,35815E+01	5,28811E+00
Substitution in positions 1-3-4	3.67809E-02	1.26470E-01	-2.73968E+00	-2,73387E-01	2,61149E+01	1,06117E+01
Substitution in positions 1-2-4-5	7.41083E-02	1.43832E-01	-1.71712E+00	2,02777E+00	4,04895E+01	1,36847E+01
Substitution in positions 1-2-3-4	5.30596E-02	1.76744E-01	-1.71712E+00	1,19331E+00	5,49143E+01	1,04805E+01
Substitution in positions 1-2-3-5	5.70868E-02	1.76744E-01	-1.71712E+00	8,74677E-01	4,24739E+01	1,30966E+01
Substitution in positions 1-2-3-4-5	-	-	-	-	6,94796E+01	1,41122E+01

Table 4 . Comparison of the accuracy between existing correlations and the proposed equations.

	n-paraffins	i-paraffins	olefins	alcyns	naphthenes	aromatics
Critical temperature		**AAD (%)**				
Proposed correlation	**0.2**	**0.3**	**0.3**	**0.8**	**0.4**	**0.4**
Joback [2]	2.3	0.5	0.6	2.2	0.5	0.4
Constantinou & al. [3]	2.1	1.7	1.7	3.2	1.6	1.1
Critical pressure		**AAD (%)**				
Proposed correlation	**7.2**	**0.5**	**3.7**	**7.1**	**11.3**	**6.5**
Joback [2]	7.8	5.6	3.6	5.0	5.9	9.2
Constantinou & al. [3]	6.9	4.8	5.2	4.9	7.2	5.0
Critical volume		**AAD (%)**				
Proposed correlation	**1.6**	**0.9**	**1.7**	**2.6**	**1.8**	**3.0**
Joback [2]	1.4	2.8	1.7	1.1	0.8	2.8
Constantinou & al. [3]	1.3	1.9	2.3	1.5	3.6	4.0
Enthalpy of vaporization		**AAD (%)**				
Proposed correlation	0.3	0.8	1.2	-	0.9	1.7
Basarova & al. [4]	6.1	2.2	2.1	-	3.4	3.0
Refractive index parameter		**AAD (%)**				
Proposed correlation	0.01	1.0	1.4	1.1	1.8	2.1
Riazi & EL-Sahhaf [5]	0.01	-	-	-	-	-
Molar volume		**AAD (%)**				
Proposed correlation	1.0	0.9	1.0	0.8	2.7	1.6
Riazi & EL-Sahhaf [5]	0.9	-	-	-	-	-

Application to Petroleum Fractions

One of the application of the proposed correlations is the prediction of petroleum fractions properties.

For simple mixtures with known compositions, their properties can be obtained by using additivity rules. In the case of petroleum fractions, the previous method can be only used for light fractions whose detailed composition can be obtained experimentally. For heavier fractions, the complexity of their composition make this procedure inapplicable. For this purpose, we have established a new procedure to estimate the average properties of this cuts by simulating each fraction by a simple mixture. In this purpose, average boiling point, liquid density at 20°C and refractive index at 20°C of the fraction are needed as initial parameters. The composition of the simulated mixture is obtained by the resolution of the following equations:

$$T_{bPF} = \sum T_{bI} \cdot X_I \qquad (3)$$
$$d_{20PF} = \sum d_{20I} \cdot X_I \qquad (4)$$
$$n_{20PF} = \sum n_{20I} \cdot X_I \qquad (5)$$

with the following constraints :

$$\sum X_I = 1 \qquad (6)$$

and $X_I \geq 0$ for all compounds I. $\qquad (7)$

The resolution of this problem was conducted as an optimisation problem by the minimization of the objective function F_{obj}.

$$F_{obj} = 100*[\sum(f_I/\theta_I)^2/N]^{0.5} \qquad (8)$$
$$f_I = \theta_{I\,(cal)} - \theta_{I\,(exp)} \qquad (9)$$
$$\text{and } \theta_{I\,(cal)} = \sum \theta_I \cdot X_I \qquad (10)$$

After the composition of the fraction is obtained, the procedure uses the group- contributions correlations to calculate the

average properties of a petroleum fraction. The additivity of each property is assumed.

The whole procedure was established as a program in MAT-LAB language.

To illustrate the established procedure, we give hereafter the results obtained for four type of petroleum fractions (light naphta, heavy naphta, kerosene and gas-oil) issued from the distillation of an Algerian crude oil.

Table 5. Data

	Light naphta	Heavy naphta	Kerosene	Gas-oil
T_b (K)	335.15	403.15	528.15	628.15
d_20	0.6735	0.7383	0.80665	0.84325
n_20	1.3812	1.4157	1.4533	1.4729

The simulated compositions given by the procedure are given in the following table.

Table 6 . Simulated Compositions

Petroleum Fraction	Components	X_I
Light naphta	3-methylpentane	1.0000
	2,2,3,4-tetramethylpentane	0.4694
Heavy naphta	2,2,4-trimethylhexane	0.3816
	1,cis-2-dimethylcyclohexane	0.1490
Kerosene	2,4-dimethyl-tridecane	1.0000
	Heneicosane	0.1419
Gas-oil	Tetradecylcyclohexane	0.0979
	Tetradecylbenzene	0.7602

Table 7 . Calculated physical Properties

	Light naphta	Heavy naphta	Kerosene	Gas-oil
Critical temperature				
Proposed method	505.7	586.3	689.3	794.6
Lee & Kesler [6]	504.5	581.1	702.4	788.0
%	*0.2*	*0.9*	*-1.9*	*0.8*
Watanasiri & al. [7]	498.5	582.9	713.7	799.7
%	*1.5*	*0.6*	*-3.4*	*-0.6*
Riazi & Daubert [8]	509.0	584.9	707.6	796.2
%	*-0.6*	*0.2*	*-2.6*	*-0.2*
Critical pressure				
Proposed method	31.8	25.4	15.5	13.1
Lee & Kesler [6]	32.5	26.9	17.8	12.5
%	*-2.1*	*-5.8*	*-13.1*	*4.3*
Watanasiri & al. [7]	27.1	23.9	16.5	10.3
%	*17.1*	*5.9*	*-6.0*	*26.8*
Riazi & Daubert [8]	33.1	26.2	17.2	12.8
%	*-3.9*	*-3.3*	*-10.0*	*2.4*
Critical volume				
Proposed method	355.6	490.4	855.4	1098.4
Riazi & Daubert [8]	390.5	502.1	819.1	1221.7
%	*-8.9*	*-2.3*	*4.4*	*-10.1*
Watanasiri & al. [7]	410.2	528.0	825.9	1200.3
%	*-13.3*	*-7.1*	*3.6*	*-8.5*
Enthalpy of vaporization				
Proposed method	27.9	34.0	47.1	58.0
Riazi & Daubert [8]	28.2	34.9	47.5	58.0
%	*-1.2*	*-2.5*	*-1.0*	*0.1*
Refractive index parameter				
Proposed method	0.228	0.252	0.260	0.285
Riazi & Daubert [8]	0.233	0.251	0.270	0.280
%	*-2.2*	*0.5*	*-3.7*	*1.7*
Molar volume				
Proposed method	129.3	169.6	275.3	331.6
Riazi & Daubert [8]	126.8	160.4	242.0	322.1
%	*2.0*	*5.7*	*13.8*	*2.9*

The results of calculation of physical properties using the group- contribution correlations are compared to other correlations recommended in literature and reported in table 7.

The previous table shows that our method gave results that are close to those obtained by other correlations recommended in the literature.

Conclusion

In this study, a group- contribution method was developed to the estimation of critical temperature, critical pressure, critical volume, enthalpy of vaporization at boiling point, refractive index parameter and molar volume of pure hydrocarbons. The proposed method is more accurate than other correlations, particularly in the case of iso- paraffins.

Besides, the proposed equations have been successfully applied to estimate the average properties of petroleum frac-tions. Our method remain valid when experimental data are lack-ing.

Nomenclature

AAD: average absolute deviation (%)

a, b, c, d, m, n, p: constants for each property in equation F.

d_{20} : liquid density at 20°C (g/cm^3)

F: mathematical function

Hv : enthalpy of vaporization at normal boiling point (kj/mole)

I : refractive index parameter [$(n^2-1)/(n^2+2)$]

M: molecular weight (g/mol)

N: number of components in a mixture

n_{20} : refractive index at 20°C

T_b: normal boiling point (K)

T_C: critical temperature (K)

P_C: critical pressure (bar)

V_C: critical volume (cm^3/mol)
V_M: molar volume at 20°C (cm^3/mol)
X :   *molar fraction*

Subscripts:
I: component I
PF: petroleum fraction
cal: calculated
exp: experimental

Greek letters
θ: a given property such as T_C, P_C,…
Δθ$_I$:   contribution of the group i for the estimation of the property θ

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