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A study of vaporization enthalpy of pure hydrocarbons

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In this research, we employed a new method to calculate vaporization enthalpy of pure hydrocarbons. This equation is a function of the temperature, far from critical point and was tested for simple mixtures and oil fractions. Comparing values with the literature, the equation established have improved results in term of average standard deviation. We also applied the equation to the oil fractions; it required a characterisation of these complex mixtures. Excellent results are obtained, which are comparable or better than those obtained with other models.

Key words: Hydrocarbons, simple mixtures, oil fractions, enthalpy of vaporization, group contribution, intramolecular interactions.

INTRODUCTION

The method of group contribution has great success and remarkable development, considering the reliability of the results which they provide. However, their application beyond the field in which they were defined can involve significant errors. To mitigate the insufficiencies of the existing methods, we set up a new correlation of group contributions with interactions, which has a better prediction of the enthalpy of vaporization of pure hydrocarbons, mixtures and oil fractions according to the temperature.

Some of the group contribution methods for estimation of enthalpy of vaporization were developed. We cite some of them: Constantinou and Gani (1994) for predicting the enthalpy of vaporization Standard 298K; Svoboda and Dockalova (1990) have proposed a group contribution equation to estimate the heat of vaporization as a function of reduced temperature. An extension of this method to other types of compounds was performed by Basarova and Svoboda (1995) who propose using the

following expression in which the terms A and α are expressed in terms of group contribution:

$$\Delta H_v = A(1 - T_r)^\alpha \exp(-\alpha T_r) \quad (1)$$

Li et al. (1997) proposed a method for estimating the enthalpy of vaporization at different temperatures by combining the principles of corresponding states and group contribution. In this method, two equations are established. The first is similar to the equation of Watson (1943) in which the term on the critical temperature is expressed as an equation group contribution. This equation requires knowledge of the enthalpy of vaporization at boiling point. The second equation is obtained by replacing the standard enthalpy of vaporization in the first equation by a relationship similar to the equation of Riedel (1954) which gives the enthalpy of vaporization at normal boiling temperature. The critical parameters that are used in this equation are evaluated for their contribution in terms of groups.

In addition to the Riedel's (1954) equation, other

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Table 1. Chemical groups.

Structural group	Characteristic
-CH ₃ -CH ₂ -	Normal paraffin
-CH< >C<	Ramified paraffin
=CH ₂ =CH- =C< =C=	Olefin
≡CH ≡C-	Alkyne compound

correlations have been proposed in the literature to estimate the enthalpy of vaporization at normal boiling temperature. Among them we cite the equations of Chen (1965) and Vetere (1973). The equations of Skander et al. (1999) based on the number of groups-CH₂-for families of hydrocarbons is presented thus:

$$\Delta H_v = a + b / \left[1 + \left((N_c) / c \right)^d \right] \quad (2)$$

a, b, c and d are constants whose values were determined in the case of n-paraffins, n-alkylcyclohexanes and n-alkylbenzenes. Meyra et al. (2004) suggested the following expression to calculate ΔH^{vap} :

$$\Delta H^{vap} = \Delta H^{vap} \frac{\left[\frac{T_c}{T_t} \right]^{Z_c} [(T_c - T) / (T_c - T_t)]^{+Z_c}}{\left[\frac{T_c - T_t}{T_c} \right]} \quad (3)$$

Where T_t is the temperature in the triple point and Z_c is the universal critical ratio. In the work of Meyra et al. (2004) the work of Guggenheim's (1945) theory was employed for determination of Z_c , which was around 0.292. In Ricardo et al. (2005), three different theories (Reid et al., 1987) were used for determination of Z_c . Three different values for Z_c (Z_{c1} : Guggenheim theory (1945) Z_{c2} : state correspondent theory; and Z_{c3} : semi-empirical value) were used in the Meyra's equation to check if it would have a marked effect in the results. The calculations have also been referenced at the normal boiling point.

The enthalpy of vaporization of simple mixtures can be determined by the rule of Kay (1936) for simple mixture expressed in molar percentages. For petroleum fractions, the method of additivity and correlations of Riazi and Daubert (1980, 1987), can be used. These last equations require knowledge of the mean-average temperature and specific-gravity of the fraction.

This article deals with the proposal of a method predicting ΔH_v , using group contribution method with interactions. Then, we apply our correlation to the mixtures, quantitatively and qualitatively known. Finally, we tested the new equation to the oil fractions, using the conventional rules of additivity.

PURE HYDROCARBONS

The steps followed for the development of the new method of group contribution with interactions is further described.

Collection data

This stage consisted of the collection data of the enthalpy of vaporization of pure hydrocarbons belonging to various chemical families starting from the data banks developed by research centers (DIPPR, 1995). This operation made it possible to collect the values of the enthalpy of vaporization in function of the temperature, far from the critical point [100 to 650K] of hydrocarbons:

$$\Delta H_v = A \left[1 - \frac{T}{T_c} \right]^B \quad (4)$$

The general equation relating ΔH_v (j/kmole) at the temperature T (K) has been given from DIPPR database (DIPPR, 1995). It is defined thus: The parameters A, B are constants that could be assessed by the method of group contribution with interactions for various families.

Definition of the structural groupings

From the established database, we preceded to the choice of the structural groups which is the most likely to contribute to the various macroscopic properties of the studied hydrocarbons. For each

families group of hydro-carbons, we have selected some chemical groups as presented in Table 1.

By choosing these groupings, we make the distinction between structural groups present in linear chains and in a cycle. For example, the contribution group-CH₂ present in n-hexane is not the same as in cyclohexane.

Definition of the principal terms of interactions between structural groups and their environments

The steps followed to introduce the terms of interactions into the correlation of group-contribution are as follows:

1. Writing the semi formula developed for each hydrocarbons family,
 2. Defining the principal terms of interactions, the hydrocarbons are characterized by their chemical nature (for example, normal paraffin C₅H₁₂) and their groups:
 - i. by the structural groups A- and -B- which are respectively CH₃- and -CH₂-, whose assembly constitutes a carbonic chain A-B-B-B-A [CH₃-CH₂-CH₂-CH₂-CH₃]
 - ii. by the principal groups of interactions A-B-B- and -B-B-B-, they are interaction terms between structural groups and their environment.
 3. Classifying, in decreasing order, the principal interaction groups number compared to the molecules number for each family.
- Tables 2 and 3 give the various principal groupings of interactions for each family of hydrocarbons. Example of principal terms of interactions between structural groupings and their environments is presented in Figures 1 to 4.

Table 2. Main groupings of interactions of the normals paraffins, isoparaffins and olefins.

Principal grouping of interaction		
n-paraffin	Isoparaffin	Olefin
CH ₃ -CH ₂ -CH ₂ -	CH ₃ -CH-CH ₂ -	-CH ₂ -CH ₂ -CH ₂ -
CH ₂ -CH ₂ -CH ₂ -	CH ₃ -CH ₂ -CH ₂ -	CH ₃ -CH ₂ -CH ₂ -
CH ₃ ...-CH ₃	CH ₃ -CH-CH ₃	-CH ₂ -CH ₂ -CH=
	-CH ₂ -CH ₂ -CH ₂ -	-CH ₂ -CH=CH ₂
	-CH ₂ -CH ₂ -CH-	CH ₃ -C-CH ₂ -
	CH ₃ -C-CH ₃	CH ₃ -C=CH ₂ -
	CH ₃ -C-CH ₂ -	-CH ₂ -CH ₂ -C=
	-CH ₂ -CH-CH ₂ -	-CH ₂ -C=CH ₂
	CH ₃ -CH ₂ -CH-	-CH ₂ -CH=CH-
	CH ₃ -CH ₂ -C-	CH ₃ -CH=CH-
	-CH ₂ -CH ₂ -C-	CH ₃ -CH-CH ₃
	CH ₃ -CH-CH-	CH ₃ -C=CH-
	CH ₃ -C-CH-	
	-CH ₂ -C-CH ₂ -	
	CH ₃ -CH-C-	
	-CH-CH ₂ -C-	
	-CH-CH-C-	

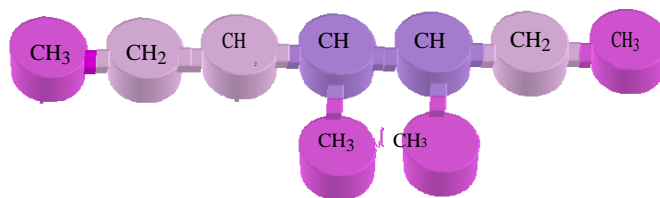


Figure 1. Isoparaffin «4,5 dimethylheptane».

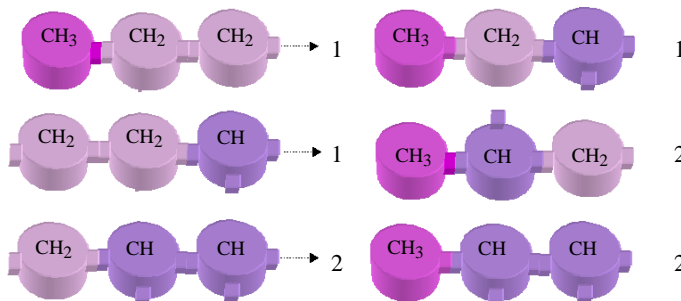


Figure 2. Number of principal groupings of interactions.

ESTABLISHMENT OF NEW CORRELATIONS OF GROUP CONTRIBUTION WITH INTERACTIONS

In our case, to establish our correlation, we test various mathematical equations stemming from the generalized form $F(\theta)$ relating the property θ , i and j types contributions, as Equation (1) shows:

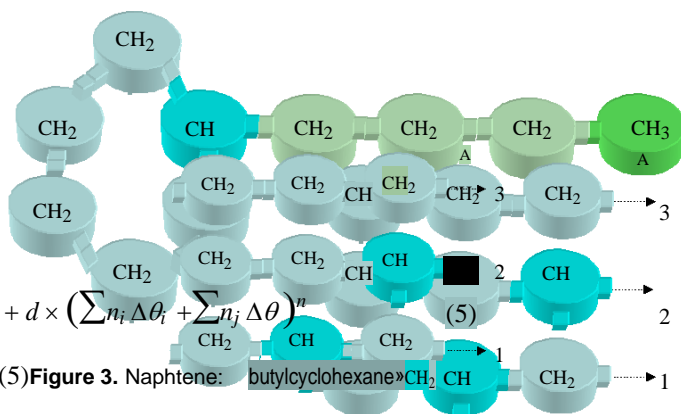
$$F(\theta) = a + b \times (\sum n_i \Delta \theta_i + \sum n_j \Delta \theta_j) + c \times (\sum n_i \Delta \theta_i + \sum n_j \Delta \theta_j)^m + d \times (\sum n_i \Delta \theta_i + \sum n_j \Delta \theta_j)^n + e \times (\sum n_i \Delta \theta_i + \sum n_j \Delta \theta_j)^p \quad (5)$$

F is a mathematical function which can take various forms as presented in Table 4. The parameters a , b , c , d , m , n and p are constants that could be assessed by the multilinear regression using the Marquardt-Levenberg algorithm. The twenty equations make it possible to test various mathematical functions and then the equation which provides the weakest variation, compared to the data of the tables taken as reference, could be selected.

With the convergence of the iterative process, the values of the parameters of the various equations are determined and their performances are evaluated by means of the average absolute deviation (AAD) compared to the values of the data bank.

Selection of new correlations

To select the best correlations among the twenty tested,



(5) Figure 3. Naphtene: butylcyclohexane

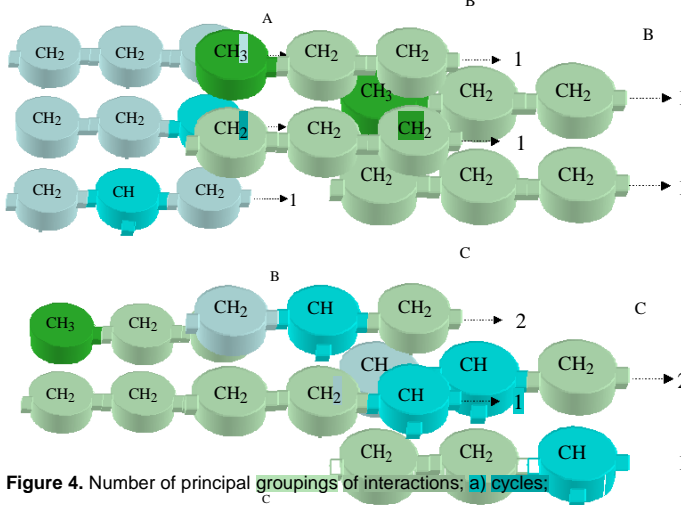


Figure 4. Number of principal groupings of interactions; a) cycles; b) ramifications; c) cycles-ramifications;

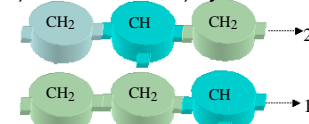


Table 3. Main groupings of interactions of naphthenes and aromatics.

Principal grouping of interaction	Cycle	Ramification	Cycle-ramification	
Naphtene	-CH ₂ -CH ₂ -CH ₂ -		CH _{3r} -CH _c -CH _{2c} -	
	-CH ₂ -CH ₂ -CH-		CH _{2r} -CH _c -CH _{2c} -	
	-CH ₂ -CH-CH ₂ -		CH _{3r} -CH _c -CH _c -	
	-CH ₂ -CH-CH-		-CH _{2r} -CH _{2r} -CH _c -	
	-CH-CH-CH-		CH _{3r} -CH _{2r} -CH _c -	
	-CH ₂ -CH ₂ -C-	CH ₃ -CH ₂ -CH ₂ -	CH _{3r} -C _c -CH _{2c} -	
	-CH ₂ -C-CH ₂ -	-CH ₂ -CH ₂ -CH ₂ -	CH _{3r} -C _c -CH _{3r} -	
	-CH ₂ -C-CH-			
	-CH ₂ -CH-C-			
	-CH-CH ₂ -CH-			
	-C-CH ₂ -CH-			
	-C-CH ₂ -C-			
	Aromatic	=CH-CH=CH-		-CH _{2r} -C-CH=
		=CH-CH=C-		-CH _{2r} -C=CH-
-CH=CH-C=		CH ₃ -CH ₂ -CH ₂ -	-CH _{2r} -CH _{2r} -C=	
-CH=C-CH=		-CH ₂ -CH ₂ -CH ₂ -	CH _{3r} -C=CH-	
-C=CH-C=			CH _{3r} -C-CH=	
-C=C-CH=			CH _{3r} -CH _r -C=	
=C-C=CH-			CH _{3r} -C=C=	
=C-C=C-			-CH _r -C-C=	

r: Ramification; c : Cycle.

Table 4. Different expressions of the F(θ) equation.

Expression	Equation
$\theta = b^*(\sum n_i \cdot \Delta\theta_i + \sum n_j \Delta\theta_j)$	(1)
$\text{Exp}(\theta/p) = b^*(\sum n_i \cdot \Delta\theta_i + \sum n_j \Delta\theta_j)$	(2)
$(1/\theta)^P = b^*(\sum n_i \cdot \Delta\theta_i + \sum n_j \Delta\theta_j)$	(3)
$(M/\theta) = b^*(\sum n_i \cdot \Delta\theta_i + \sum n_j \Delta\theta_j)$	(4)
$(T_b/\theta) = b^*(\sum n_i \cdot \Delta\theta_i + \sum n_j \Delta\theta_j)$	(5)
$\theta = a + b^*(\sum n_i \cdot \Delta\theta_i + \sum n_j \Delta\theta_j)$	(6)
$\text{Exp}(\theta/p) = a + b^*(\sum n_i \cdot \Delta\theta_i + \sum n_j \Delta\theta_j)$	(7)
$(1/\theta)^P = a + b^*(\sum n_i \cdot \Delta\theta_i + \sum n_j \Delta\theta_j)$	(8)
$(M/\theta) = a + b^*(\sum n_i \cdot \Delta\theta_i + \sum n_j \Delta\theta_j)$	(9)
$(T_b/\theta) = a + b^*(\sum n_i \cdot \Delta\theta_i + \sum n_j \Delta\theta_j)$	(10)
$\theta = a + b^*(\sum n_i \cdot \Delta\theta_i + \sum n_j \Delta\theta_j) + c^*(\sum n_i \cdot \Delta\theta_i + \sum n_j \Delta\theta_j)^m$	(11)
$\text{Exp}(\theta/p) = a + b^*(\sum n_i \cdot \Delta\theta_i + \sum n_j \Delta\theta_j) + c(\sum n_i \cdot \Delta\theta_i + \sum n_j \Delta\theta_j)^m$	(12)
$(1/\theta)^P = a + b^*(\sum n_i \cdot \Delta\theta_i + \sum n_j \Delta\theta_j) + c(\sum n_i \cdot \Delta\theta_i + \sum n_j \Delta\theta_j)^m$	(13)
$(M/\theta) = a + b^*(\sum n_i \cdot \Delta\theta_i + \sum n_j \Delta\theta_j) + c(\sum n_i \cdot \Delta\theta_i + \sum n_j \Delta\theta_j)^m$	(14)
$(T_b/\theta) = a + b^*(\sum n_i \cdot \Delta\theta_i + \sum n_j \Delta\theta_j) + c(\sum n_i \cdot \Delta\theta_i + \sum n_j \Delta\theta_j)^m$	(15)
$\theta = a + b^*(\sum n_i \cdot \Delta\theta_i + \sum n_j \Delta\theta_j) + c(\sum n_i \cdot \Delta\theta_i + \sum n_j \Delta\theta_j)^m + d(\sum n_i \cdot \Delta\theta_i + \sum n_j \Delta\theta_j)^n$	(16)
$\text{Exp}(\theta/p) = a + b^*(\sum n_i \cdot \Delta\theta_i + \sum n_j \Delta\theta_j) + c(\sum n_i \cdot \Delta\theta_i + \sum n_j \Delta\theta_j)^m + d(\sum n_i \cdot \Delta\theta_i + \sum n_j \Delta\theta_j)^n$	(17)
$(1/\theta)^P = a + b^*(\sum n_i \cdot \Delta\theta_i + \sum n_j \Delta\theta_j) + c(\sum n_i \cdot \Delta\theta_i + \sum n_j \Delta\theta_j)^m + d(\sum n_i \cdot \Delta\theta_i + \sum n_j \Delta\theta_j)^n$	(18)
$(M/\theta) = a + b^*(\sum n_i \cdot \Delta\theta_i + \sum n_j \Delta\theta_j) + c(\sum n_i \cdot \Delta\theta_i + \sum n_j \Delta\theta_j)^m + d(\sum n_i \cdot \Delta\theta_i + \sum n_j \Delta\theta_j)^n (T_b/\theta) =$	(19)
$a + b^*(\sum n_i \cdot \Delta\theta_i + \sum n_j \Delta\theta_j) + c(\sum n_i \cdot \Delta\theta_i + \sum n_j \Delta\theta_j)^m + d(\sum n_i \cdot \Delta\theta_i + \sum n_j \Delta\theta_j)^n$	(20)

we retained for each parameter (A and B) the equations, having provided relatively the weakest variations compared to the bench-mark data for each family of hydrocarbon. We select Equation (11) for parameter "A" (AAD% = 1.29%) and Equation (19) (AAD% = 2.23%) for the parameter "B".

The values of the parameters A and B of the normal paraffin, isoparaffin, olefin, naphtene and aromatic are given in Tables 5 and 6.

Validity of the correlation

Once this stage of determination of parameters A and B of the general equation ($\Delta H_V = A (1-(T/T_C))^B$) is completed, we carried out the calculation of the enthalpy of vaporization of pure hydrocarbons.

We tested the correlation for two temperatures (298,15 K and T_{eb}) so that to check the validity of our correlation whatever the selected temperature. Absolute average deviations obtained by comparing the enthalpy of vaporization calculated by our correlation and that found in the data bank of "DIPPR" (1995) (ΔH_V of reference) are recorded in Table 7.

The variations recorded by our method compared to the reference are very weak. In the same way, we note that the variation in the temperature does not influence the validity of the proposed method.

Comparison between the correlations established and other correlations of the literature

In this research, in order to further test the reliability of the suggested correlation, a study was undertaken by carrying out a comparison based on the AAD recorded by various methods available in the literature and the current correlation referring to the data bank for the five studied families of hydrocarbons.

We compared our correlation with correlation of Pitzer et al. (1955), Basarova and Svoboda (1995), and Vetere (1973). We also compared with the correlation of Ricardo (2005) using the correlation of Meyra et al. (2004), we note that the differences are greater than 20%, so we changed the correlation Meyra et al. (2004) with adding the term k:

$$\Delta H^{vap} = k \Delta H_t^{vap} \left| \frac{c}{I_c - I_t} \right| \quad (6)$$

$$\left[\frac{T - T_c}{T_c} \right]^{Z_c} \left[\frac{T - T_i}{T_c} \right]^{+Z_c}$$

With: $k = 3Z_c$

Comparison of deviations recorded by the general equation established and correlations Pitzer et al. (1955),

Basarova and Svoboda (1995), Vetere (1973) and Ricardo (2005) are given in Table 8.

According to Table 8, the selected correlation gave weak variations compared to the reference at the normal boiling point and the other correlations for all the studied hydrocarbons families. In addition, The H_{vb} calculated from the established correlation remains close to that given by the reference.

APPLICATION FOR SIMPLE MIXTURES

Twenty binary and ternary mixtures each, whose components belong either to the same family or to different families, were examined. Initially, the evaluation consists in the calculation of the different mixtures components properties; secondely, the mixture average property was determined; finally, the obtained results were compared with literature:

$$\Delta H_{vm} = \frac{\sum \Delta H_{vi} * X_i}{\sum X_i} \quad (7)$$

With: ΔH_{vm} : enthalpy of vaporization of the mixture in kj/mole; ΔH_{vi} : enthalpy of vaporization of component «i» in the mixture (kj/mole); X_i : molar fraction of component «i».

Binary mixtures

The binary mixtures that we have studied are represented in the following Table 9. The results obtained during the calculation of the enthalpy of vaporization of the twenty (20) binary mixtures at 298,15K are represented in the following Table 10.

By analyzing the results represented in the Table 10, we note that the absolute average deviations recorded by our correlation are weaker, compared to those obtained by the method of Pitzer and this for all the studied mixtures. Therefore, our correlation remains successfully applicable to binary mixtures.

Ternary mixtures

We applied the same calculations to ternary mixtures whose compositions are shown in Table 11. The results obtained during the calculation of the enthalpy of vaporization of the 20 ternary mixtures at 298,15 K are represented in Table 12.

According to results from Table 12, compared to the correlation of Pitzer, the suggested correlation raised weaker variations for the majority of the studied mixtures. Therefore the established correlation for pure hydrocarbons applies correctly to ternary mixtures.

Table 5. Parameters of the selected correlations of group contribution with interactions for parameter A.

n-paraffin : Equation 11		Isoparaffin : Equation 11	
Parameter		Parameter	
a	-1602676.75	a	10158146.1
b	14.1088334	b	16.4382549
c	9375.83247	c	15261.1611
m	0.42073779	m	0.46828699
Structural groupings		Structural groupings	
-CH ₃	306279.945	-CH ₃	164454.822
-CH ₂ -	161958.05	-CH ₂ -	93320.7788
		-CH<	430229.691
		>C<	306635.302
Principal groupings of interactions		Principal groupings of interactions	
CH ₃ -CH ₂ -CH ₂ -	306279.945	CH ₃ -CH-CH ₂ -	-39332.5498
-CH ₂ -CH ₂ -CH ₂ -	2184463.261	CH ₃ -CH-CH ₃	7922.22325
-CH ₃ ...-CH ₃	612558.89	CH ₃ -CH ₂ -CH ₂ -	205730.41
		-CH ₂ -CH ₂ -CH-	-15433.7278
		CH ₃ -C-CH ₃	128223.231
		CH ₃ -CH ₂ -CH-	96423.4456
		-CH ₂ -CH ₂ -CH-	20643.9093
		CH ₃ -C-CH ₂ -	8369.29125
		-CH ₂ -CH-CH ₂ -	-68031.6205
		CH ₃ -CH-CH-	206113.841
		-CH ₂ -CH ₂ -CH ₂ -	2819.22875
		-CH ₂ -CH-CH-	43622.6622
		CH ₃ -C-CH-	104740.089
		CH ₃ -CH ₂ -C-	-143556.96
		-CH ₂ -CH ₂ -C-	83425.825
		-CH ₂ -C-CH ₂ -	54943.2509
		-CH ₂ -C-CH-	69440.8828

APPLICATION OF THE METHOD ESTABLISHED TO OIL FRACTIONS

In this part of our work, we applied the correlations established to some oil fractions (light, averages and heavy) from an Algerian crude oil.

Case of the light oil fractions

For this type of fractions, we apply the same step exactly as that adopted for simple mixtures, since the quantitative and qualitative composition of the fractions is known. We use the following relation:

$$\Delta H_{Vfp} = \frac{\sum v_i \Delta H_i}{\sum X_i} \quad (8)$$

With: ΔH_{Vfp} : enthalpy of vaporization of oil fractions in kJ/mole; ΔH_{Vi} : enthalpy of vaporization of component « i » in oil fraction (kJ/mole); X_i : molar fraction of component « i ».

Average and heavy oil fractions

We observed the rule of additivity and the assumption of the pseudo-components (hypothetical hydrocarbon) as follows:

While basing itself on the molar mass of the oil fraction

Since the oil fractions contain practically only three

Table 6. Parameters of the selected correlations of group contribution with interactions for parameter B.

n-paraffin : Equation 19		Isoparaffin : Equation 19		Olefin : Equation 11	
Parameter	Value	Parameter	Value	Parameter	Value
a	28.0053459	a	28.215093	a	4399888.55
b	82.8886734	b	85.516316	b	26079.5318
c	-943.091941	c	-337.291074	c	261221.607
m	-3.20182293	m	-2.27143952	m	0.1858332
d	-943.091941	d	-337.291074		
n	-3.20182293	n	-2.27143952		
Structural grouping	Value	Structural grouping	Value	Structural grouping	Value
-CH ₃	0.66241163	-CH ₃	0.89485725	-CH ₃	261.969421
-CH ₂ -	0.7391905	-CH ₂ -	0.53841215	-CH ₂ -	256.308434
		-CH<	-0.4954034	-CH<	405.309306
		>C<	-0.9173492	>C<	220.10477
				=CH ₂	251.396698
				=CH=C<	238.561754
Principal grouping of interactions	Value	Principal grouping of interactions	Value	Principal grouping of interactions	Value
CH ₃ -CH ₂ -CH ₂ -	-0.33779364	CH ₃ -CH-CH ₂ -	0.01719311	-CH ₂ -CH ₂ -CH ₂ -	-55.7753987
-CH ₂ -CH ₂ -CH ₂ -	-0.4523436	CH ₃ -CH-CH ₃	0.03450571	CH ₃ -CH ₂ -CH ₂ -	-11.6329586
-CH ₃ ...-CH ₃	0.32456277	CH ₃ -CH ₂ -CH ₂ -	-0.27999073	-CH ₂ -CH ₂ -CH=	-51.643278
		CH ₃ -C-CH ₃	0.00632537	-CH ₂ -CH=CH ₂	119.895742
		-CH ₂ -CH ₂ -CH-	-0.15324476	CH ₃ -CH=CH-	51.7924179
		-CH ₂ -CH ₂ -CH-	-0.14058059	-CH ₂ -CH=CH-	51.7924179
		CH ₃ -C-CH ₂ -	-0.0233563	CH ₃ -CH ₂ -CH=	6.05591567
		-CH ₂ -CH-CH ₂ -	-0.04548205	CH ₃ -CH-CH ₃	-234.604872
		CH ₃ -CH-CH-	0.07576622	CH ₃ -C=CH-	-7.69474981
		-CH ₂ -CH ₂ -CH ₂ -	-0.25785315	CH ₃ -C-CH ₃	30.853715
		-CH ₂ -CH-CH-	0.03691472	CH ₃ -CH-CH=	13.4378487
		CH ₃ -C-CH-	-0.05359021	CH ₃ -C-CH ₂ -	11.4714888
		CH ₃ -CH ₂ -C-	-0.1727451	CH ₃ -C=CH ₂ -	11.4135532
		CH ₃ -CH-C-	0.16585181	Terms of position	
		-CH ₂ -CH ₂ -C-	-0.22570371	Cis	-68.4092800
				Trans	-67.6778359
		Naphtene : Equation 11		Aromatic : Equation 11	
		Parameter	Value	Parameter	Value
		a	16282193.3	a	-15647428.6
		b	22.1665989	b	-4.81131743
		c	12959.8011	c	68852.1317
		m	0.5319444	m	0.50474669
		Structural grouping	Value	Structural grouping	Value
		-CH ₃	44398.1163	-CH ₃	53175.9389
		-CH ₂ -	34389.882	-CH ₂ -	271456.811
		-CH<	42917.0212	-CH<	302109.982
		>C<	116771.968	>C<	477111.553
				=CH-	43757.8544
				=C<	45563.544

Table 6. Contd.

Principal grouping of interaction		Value	Principal grouping of interaction		Value
Cycle-Ramification	-CH _{2r} -CH _c -CH _{2c}	79670.3701	Cycle - Ramification	-CH _{2r} -C-CH=	21889.4097
	-CH _{2r} -CH _{2r} -CH _c	72271.4972		-CH _{2r} -C=CH-	-13316.1082
	CH _{3r} -CH _c -CH _{2c}	14607.2621		CH ₃ -C=CH-	88422,5709
	CH _{3r} -CH _c -CH _c	14381.1117		CH ₃ -C-CH=	12670,3175
Ramification	CH ₃ -CH ₂ -CH ₂ -	72271.4972	Ramification	CH ₃ -CH ₂ -CH ₂ -	-110214.647
	-CH ₂ -CH ₂ -CH ₂ -	131518.705		-CH ₂ -CH ₂ -CH ₂ -	-16309.7454
Cycle	-CH ₂ -CH ₂ -CH ₂	89640,2866	Cycle	=CH-CH=CH-	82620,6895
	-CH ₂ -CH ₂ -CH-	35973,1679		=CH-CH=C-	26541,2225
	-CH ₂ -CH-CH ₂ -	61990,6156		-CH=CH-C=	173008,653
	-CH ₂ -CH-CH-	14381,1117		-CH=C-CH=	32624,6607
	-CH ₂ -CH ₂ -C-	58385,4839		-C=CH-C=	136287,196
	-CH ₂ -C-CH ₂ -	116770,968		-C=C-CH=	46436,9893
	-CH-CH ₂ -CH-	3385,09777		=C-C=CH-	159008,901
			=C-C=C-	168317,541	
Terms of position		Value			
Cis		159457.069			
Trans		142117.832			

Table 7. Average absolute deviations (AAD%) recorded by the general equation for the calculation of the enthalpy of vaporization of pure hydrocarbons.

Interval	Family	n-paraffin	Isoparaffin	Olefin	Naphtene	Aromatic	AAD%
		C ₅ -C ₁₉	C ₅ -C ₉	C ₅ -C ₂₀	C ₆ -C ₁₆	C ₆ -C ₂₄	-
Nb pts		15	35	25	18	35	128
Suggested correlation at 298,15 K		0.8	0.95	0.83	0.46	1.06	0.87
Suggested correlation at T _{eb}		0.69	0.86	0.4	0.52	1.28	0.82

Table 8. Comparison between the established correlation and correlations Pitzer et al. (1955), Basarova and Svoboda (1995), Vetere (1973) and Ricardo (2005) at the normal boiling point.

Interval	Family	n-paraffin	Isoparaffin	Olefin	Naphtene	Aromatic	AAD %
		C ₅ -C ₁₉	C ₅ -C ₉	C ₅ -C ₂₀	C ₆ -C ₁₆	C ₆ -C ₂₄	-
Nb pts		15	35	25	18	35	128
Suggested correlation		0.69	0.86	0.4	0.52	1.28	0.82
Pitzer		5.57	3.04	4.62	5.78	4.33	4.38
Svoboda		3.08	1.76	1.58	1.42	4.94	2.70
Vetere		2.44	1.23	0.90	1.72	1.94	1.57
Nb pts		15	27	25	16	35	119
Ricardo et al.	Z _{c1} =0.292	16.12	11.72	15.22	11.73	15.51	14.03
	Z _{c2} =0.27	6.87	3.97	4.32	3.06	5.81	4.79
	Z _{c3}	2.01	3.68	3.95	4.01	4.27	3.71

Table 9. List studied of binary mixtures.

No. of the mixture	Components "1"	Components "2"
1	Hexane	Heptane
2	Benzene	Toluene
3	Hexane	Cycloheptane
4	Benzene	Cycloheptane
5	Hexane	Benzene
6	Tridecane	Tetradecane
7	Pentadecane	Heptane
8	Heptane	Methylcyclohexane
9	Heptane	Ethylbenzene
10	Ethylbenzene	Hexane
11	Ethylbenzene	Nonane
12	methylcyclohexane	Heptane
13	Hexane	Nonane
14	Hexane	Heptane
15	Hexane	Heptane
16	Tetradecane	Hexane
17	Hexane	Decane
18	Benzene	Toluene
19	Benzene	Cycloheptane
20	Heptane	Methylcyclohexane

families of hydrocarbons: aromatic paraffins and naphthenes, we compare our oil fractions to mixtures of these three families by using the following additivity rule:

$$\Delta H_{VFP} = \Delta H_{VP} * X_P + \Delta H_{VN} * X_N + \Delta H_{VA} * X_A \quad (9)$$

With: X_P , X_N and X_A : molar compositions of the fraction in: aromatic paraffins, naphthenes respectively; ΔH_{VP} , ΔH_{VN} and ΔH_{VA} : enthalpies of vaporizations of paraffin, naphtene and the aromatic (pure hydrocarbons) respectively having the same molar mass as the oil fraction.

The characteristics of the fractions used for the application of our correlation are gathered in Table 13. For the calculation of the composition of the oil fractions, we used the following Riazi-Daubert [12, 13] correlation:

For $MM < 200$ g/mol (light and average molar fractions)

$$X_P = 373,87 - 408,29SpGr + 1,4772m$$

$$X_N = -150,27 + 210,152SpGr - 2,388m$$

$$X_A = 100 - (X_P + X_N)$$

For $MM > 200$ g/mol (heavy fractions)

$$X_P = 198,42 - 27,772Ri - 15,643CH$$

$$X_N = 59,77 - 76,174Ri + 6, < 8048CH$$

$$X_A = 100 - (X_P + X_N)$$

$$\text{With: } m = M(n_{20} - 1,4750); Ri = \frac{n - d}{20 - 20,2}$$

The results obtained are given in Table 14. For the light fraction, the mass molar is given by CPG. But for the average and the heavy fractions, it is calculated by the method of Riazi-Daubert; X_i : Composition of the various families obtained by the method of Riazi-Daubert (Riazi and Daubert. 1980, 1987),

Light fractions

First fraction

For the light fractions, we have the quantitative and qualitative composition obtained by CPG, as shows in Table 15.

We compared the results with the reference. They are recorded in Table 16. The results of the enthalpy of vaporization of the studied light fraction show that our equations are very close to the reference. This result was predictable because the enthalpy of vaporization of the fraction was calculated starting from a detailed composition and the correlations established in the case of pure hydrocarbons are very efficient.

Average fractions

Using the characterization based on the molar mass (MM)

For the second fraction, we suppose that the oil fraction can be comparable as normal paraffin at first, then as naphthen and finally, as aromatic, which has the same molar mass as the cut that we have to treat. Compounds corresponding:

- i. n-nonane for normal paraffin,
- ii. n-propylcyclohexane for naphthen,
- iii. n-propylbenzene for aromatic.

The values of each family of enthalpy of vaporization are calculated by the correlation suggested:

$$\Delta H_{VP} = 37,55 \text{ kj / mol}$$

$$\Delta H_{VN} = 35,44 \text{ kj / mol}$$

$$\Delta H_{VA} = 36,27 \text{ kj / mol}$$

Where the value of the enthalpy of vaporization of the oil fraction can be calculated as follows:

$$\Delta H_{VFP} = \Delta H_{VP} * X_P + \Delta H_{VN} * X_N + \Delta H_{VA} * X_A$$

With: $X_P = 52.30$; $X_N = 23.35$; $X_A = 24.35$

Table 10. AAD (%) recorded by the established correlation and other methods for the calculation of binary mixtures.

Mixture N°	Composition % molar		Reference value (KJ/mole)	Proposed correlation (KJ/mole)	Pitzer (KJ/mole)	% AAD	
	% mol ₁	% mol ₂				Proposed correlation	Pitzer
1	44	56	34.3904	34.6176	33.7644	0.66	1.82
2	45	55	36.0875	36.1545	35.4380	0.19	1.80
3	46	54	34.6072	34.6754	31.7310	0.20	8.31
4	55	45	35.3115	35.3015	32.6285	0.03	7.60
5	45	55	32.7555	32.8220	32.1110	0.20	1.97
6	48	52	68.2376	67.7520	63.1236	0.71	7.49
7	36	64	50.5980	50.4604	47.6508	0.27	5.82
8	44	56	36.0196	36.1876	35.1948	0.47	2.29
9	44	56	39.7604	40.0012	38.9356	0.61	2.07
10	62	38	38.1616	38.3526	37.4650	0.50	1.83
11	55	45	39.2140	39.3655	38.3540	0.39	2.19
12	56	44	33.7800	33.8952	33.1092	0.34	1.99
13	68	32	36.2216	36.4904	35.4972	0.74	2.00
14	17	83	35.7647	36.0243	35.0442	0.73	2.01
15	71	29	33.0161	33.2109	32.4846	0.59	1.61
16	38	62	46.3296	46.2388	43.8552	0.20	5.34
17	35	65	44.1045	44.5050	42.9075	0.91	2.71
18	17	83	37.2775	37.3837	36.7148	0.28	1.51
19	80	20	34.4440	34.4340	32.7960	0.03	4.78
20	65	35	36.2485	36.4585	35.4405	0.58	2.23
% AAD Average						0.43	3.37

Table 11. Composition of ternary mixtures.

No. of the mixture	Component "1"	Component "2"	Component "3"
1	Hexane	Heptane	Nonane
2	Hexane	Tetradecane	Tetradecane
3	Ethylcyclohexane	Benzene	Hexane
4	Cycloheptane	Toluene	Heptane
5	Heptane	Benzene	Toluene
6	Heptane	Ethylcyclohexane	Ethylcyclopentane
7	Tridecane	Tridecane	Ethylcyclohexane
8	Benzene	Toluene	Ethylbenzene
9	Benzene	Ethylbenzene	Tridecane
10	Benzene	Ethylbenzene	Ethylcyclopentane
11	Heptane	Tridecane	Hexane
12	Tridecane	Ethylcyclohexane	Benzene
13	Heptane	Decane	Ethylcyclopentane
14	Decane	Ethylcyclohexane	Ethylcyclopentane
15	Decane	Benzene	Toluene
16	Décane	Toluene	Ethylbenzene
17	Tridecane	Cycloheptane	Toluene
18	Tridecane	Ethylcyclohexane	Ethylbenzene
19	Benzene	Toluene	Hexane
20	Benzene	Toluene	Ethylcyclopentane

Table 12. AAD (%) recorded by the suggested method and other methods for the calculation of the ternary mixtures.

Mixture No.	Composition % molar			Reference value (kJ/mole)	Proposed correlation (kJ/mole)	Pitzer correlation (kJ/mole)	% AAD	
	%mol ₁	%mol ₂	%mol ₃				Proposed correlation	Pitzer
1	27	32	41	39.17	39.50	38.25	0.86	2.35
2	17	43	40	61.85	61.48	57.58	0.61	6.91
3	34	34	32	35.37	35.37	33.96	0.00	3.97
4	27	39	34	37.32	37.47	35.52	0.38	4.83
5	31	31	38	36.26	36.39	35.57	0.37	1.90
6	32	30	38	37.90	37.99	36.38	0.25	4.01
7	37	43	20	62.50	62.08	57.89	0.66	7.37
8	20	36	44	39.01	39.14	38.28	0.35	1.86
9	15	60	25	46.85	46.86	45.12	0.01	3.69
10	19	62	19	39.59	39.74	38.70	0.38	2.24
11	26	52	22	50.69	50.56	48.13	0.27	5.06
12	48	24	28	50.79	50.53	47.77	0.52	5.95
13	15	49	36	43.69	44.03	42.40	0.79	2.94
14	44	27	29	44.03	44.26	42.23	0.52	4.09
15	40	28	32	41.96	42.21	40.92	0.60	2.47
16	37	29	34	44.20	44.50	43.16	0.69	2.34
17	24	58	18	44.23	44.13	40.21	0.22	9.08
18	19	16	65	46.45	46.47	44.59	0.05	3.99
19	29	28	43	33.99	34.09	33.42	0.30	1.66
20	23	23	54	36.40	36.49	35.53	0.25	2.40
% AAD Average							0.40	3.96

Table 13. Characteristics of the studied oil fractions.

Fraction		T _{mav} (°C)	SpGr	Kuop
Light	1 Cut C ₅ -80°C	52.67	0.6595	12.65
	2 Cut 155-160°C	157.5	0.7689	11.94
Average	3 Cut 195-200°C	197.5	0.7926	11.94
	4 Cut 250-260°C	255.0	0.8211	11.98
Heavy	5 Cut 270-280°C	275.0	0.8352	11.92
	6 Cut 310-320°C	315.0	0.8615	11.83
	7 Cut 350-360°C	355.0	0.8795	11.91

Kuop: Factor of characterization of Watson; SpGr: specific gravity; T_{mav}: average boiling point of the oil fraction.

Table 14. Characteristics of the oil fractions.

Fraction		MM (g/mole)	% X _P	% X _N	% X _A
Light	1 Cut C ₅ -80°C	69.39	-	-	-
	2 Cut 155-160°C	122	52.30	23.35	24.35
Average	3 Cut 195-200°C	143	44.37	25.82	29.81
	4 Cut 250-260°C	186	35.81	26.83	37.36
Heavy	5 Cut 270-280°C	201	68.57	23.05	8.38
	6 Cut 310-320°C	236	65.12	24.57	10.31
	7 Cut 350-360°C	280	64.01	25.14	10.85

MM: mass molar of the oil fractions.

Table 15. Composition of the fraction C₅ -80°C.

No.	Name of constituent	% Molar
1	Iso butane	0.01
2	n-butane	0.16
3	Iso pentane	19.15
4	n-pentane	18.99
5	2,2-dimethyl butane	2.30
6	cyclopentane	0.57
7	2,3-dimethyl butane	3.18
8	2-methyl pentane	14.65
9	3-methyl pentane	8.37
10	n-hexane	16.99
11	Methyl cyclo pentane	3.17
12	2,2-dimethyl pentane	1.16
13	Benzene	4.34
14	3,3-dimethyl pentane	0.15
15	cyclohexane	2.70
16	2-methyl hexane	1.50
17	2,3-dimethyl pentane	0.58
18	3-methyl hexane	1.07
19	1-cis-3-dimethyl cyclo pentane	0.09
20	1-trans-3-dimethyl cyclo pentane	0.12
21	3-ethyl pentane	0.16
22	n-heptane	0.44
23	Methyl cyclo hexane	0.15
Total		100.00

Table 16. Results obtained for the fraction N°1.

N°1 fraction	ΔH_v	% AAD
Reference	27.66	
Established correlation	27.50	0.58
Riazi-Daubert	27.35	1.12

One obtains $\Delta H_{vFP} = 36.75$ kJ/mole (suggested correlation) and the enthalpy of vaporization of reference is $\Delta H_{vFP} = 35.15$ kJ/mole. We precede in the same way for the 3 other fractions and the results obtained are gathered in Table 17.

According to the results gathered in Table 18, we notice that our method gave weaker variations than those obtained by the correlation of Riazi-Daubert which presents itself relatively weak deviations compared to the reference.

Heavy fractions

In the case of this type of fractions, the qualitative and quantitative composition is not known. We use the method of the pseudo-compound in order to calculate the

enthalpy of vaporization of these heavy fractions by the suggested correlation. We compare the results with the reference and the method of Riazi-Daubert.

Concerning the heavy fractions, we observe that the variations obtained by our correlation are relatively weakest compared to the reference. We can conclude that the correlation established for pure hydrocarbons also apply properly to oil fractions (average and heavy).

Conclusion

The present research was conducted to enrich the list by the existing empirical methods in the literature and aimed at approaching the thermodynamic properties, according to the temperature of pure hydrocarbons and their mixtures, in oil fractions.

These methods make it possible to avoid the recourse to experimental handling which is not always realizable.

The results obtained showed that the established correlation is reliable and presents weak variations compared to bank data for pure hydrocarbons. It is also applied to simple mixtures and oil fractions using the rule of additivity.

Compared with other correlation of the literature, our

Table 17. Calculated enthalpy of vaporization of the average fractions.

Variable	FP2	FP3	FP4
MM (g/mole)	122	143	186
n-parrafin	n-nonane	n-decane	n-tridecane
ΔH_{VP} (Reference)	37.32	39.60	46.53
ΔH_{VP} (Estimated)	37.55	39.94	46.26
Naphtene	n-propylcyclohexane	n-butylcyclohexane	n-heptylcyclohexane
ΔH_{VN} (Reference)	35.83	37.93	40.61
ΔH_{VN} (Estimated)	35.44	38.26	41.18
Aromatic	n-propylbenzene	n-pentylbenzene	octylbenzene
ΔH_{VA} (Reference)	38.07	42.47	47.78
ΔH_{VA} (Estimated)	36.27	42.06	48.22
% P	52.30	44.37	35.81
% N	23.35	25.82	26.83
% A	24.35	29.81	37.36
ΔH_{VFP} (Reference)	37.15	40.02	45.41
ΔH_{VFP} (Estimated)	36.75	40.14	45.63

Table 18. Variations recorded for the average fractions by our correlation and Riazi-Daubert correlation.

FP	ΔH_{VFP} (Reference) (KJ/mole)	ΔH_{VFP} (Estimated) (KJ/mole)	Riazi-Daubert correlation (KJ/mole)	% AAD	
				Suggested correlation	Riazi-Daubert
FP 2	37.15	36.75	37.65	1.08	1.35
FP 3	40.02	40.14	41.68	0.30	4.15
FP 4	45.41	45.63	47.55	0.48	4.71

Table 19. Calculated enthalpy of vaporization of the heavy fractions.

Variable	FP5	FP6	FP7
MM (g/mole)	201	236	280
n-Parrafin	n-Tetradecane	n-Heptadecane	n-Eicosane
ΔH_{VP} (Reference)	47.88	53.53	56.45
ΔH_{VP} (Estimated)	48.10	53.09	57.38
Naphtene	n-Nonylcyclopentane	Dodecylcyclopentane	Tetradecylcyclohexane
ΔH_{VN} (Reference)	51.75	58.13	64.89
ΔH_{VN} (Estimated)	50.82	58.85	65.40
Aromatic	n-Nonylbenzene	Undecylbenzene	Tetradecylbenzene
ΔH_{VA} (Reference)	45.16	54.21	59.28
ΔH_{VA} (Estimated)	49.91	53.32	58.11
% P	68.57	65.12	64.01
% N	23.05	24.57	25.14
% A	8.38	10.31	10.87
ΔH_{VFP} (Reference)	48.54	54.73	58.89
ΔH_{VFP} (Estimated)	48.88	54.53	59.49

Table 20. Variations recorded for the heavy fractions by our correlation and Riazi-Daubert correlation.

FP	ΔH_{VFP} (Reference) (KJ/mole)	ΔH_{VFP} (Estimated) (KJ/mole)	Method of Riazi-Daubert (KJ/mole)	% AAD	
				Suggested correlation	Riazi-Daubert
FP 5	48.54	48.88	49.62	0.70	2.22
FP 6	54.73	54.53	53.78	0.37	1.74
FP 7	58.89	59.49	57.99	1.02	1.53

Notations

AAD, Average absolute deviation (%); a, b, c, d, m, n and p, parameters of the equations of group contribution with interactions; A and B, parameters of the equation of the enthalpy of vaporization; n_i , number of structural groups of type "i"; n_j , number of principal groups of interactions of the type "j"; ΔH_v , enthalpy of vaporization; ΔH_{VM} , enthalpy of vaporization of the mixture; ΔH_{Vfp} , enthalpy of vaporization of the oil fraction; ΔH_{Vi} , enthalpy of vaporization of component i; X_i , molar fraction of component i; T_c , critical temperature; T_{eb} , boiling point; R, constant of perfect gases; K_{uop} , factor of characterization of Watson; d_{20} , density with 20°C; n_{20} , index of refraction at 20°C; MM, molar mass; SpGr, specific-gravity; DIPPR, Design Institute for Physical Property data.

Greek letters

Θ , Parameters of the studied property; $\Delta\theta_i$, contribution of the structural group of type "i"; $\Delta\theta_j$, contribution of the principal group of interaction of the type "j".

Indices

A, Aromatic; N, naphthenic; P, paraffin; FP, oil fraction; eb, boiling; C, critical; I, a component in the mixture; mav, mean average; mol, molar.

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