# CONTRIBUTION TO THE STUDY OF THE THERMODYNAMICAL PROPERTIES OF ALGERIAN CRUDE OIL WITH THE USE OF DIFFERENT NUMERICAL METHODS 

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$$
\begin{align*}
& \text { الالاصــة : } \\
& \text { باستخدام الماسوب أمكن اكتشافـ بعض الوظائف الفيزيائية والكييائية للأجسام المالصة للأجزاء } \\
& \text { البترولية . وقد اكتفت هذه الدراسة بالتوقف عند الأجزاء الحفيفية ( من خمسة إلى عشرة ذرّة الكر بون } \\
& \text { كالفحم العطري أو البرقيني أو النفتيني }
\end{align*}
$$


#### Abstract

It is not always easy to measure experimentally certain physical or chemical properties of pure components of petroleum fractions. This had led us to develop equations which, with the help of the computer, enabled us to estimate these properties when at least one of them is known. Our study was limited to the $\mathrm{C}_{5}$ to $\mathrm{C}_{10}$ components of the light fractions.

Further, we propose two correlations from which the fractional composition of paraffins, naphthenes, and aromatics contained in petroleum fractions can be derived.


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## NOTATION

$T_{\mathrm{b}}$ Boiling point at 1 atm in ${ }^{\circ} \mathrm{C}$
$C_{g}$ Freezing point at 1 atm in K
$d$ Density of the liquid in $\mathrm{g} \mathrm{ml}^{-1}$
$n$ Refractive index of the liquid
$V_{\mathrm{A}}$ Absolute viscosity at $25^{\circ} \mathrm{C}$ in centipoise
$T_{\mathrm{s}}$ Surface tension of the liquid at $25^{\circ} \mathrm{C}$ in dyn $\mathrm{cm}^{-1}$
$H_{\mathrm{v}}$ Heat of vaporization at saturation pressure in cal g ${ }^{-1}$
$H_{c}$ Heat of combustion of the liquid at $25^{\circ} \mathrm{C}$ and constant pressure in $\mathrm{kcal} \mathrm{mol}^{-1}$
$C_{\mathrm{p}}$ Heat capacity at $25^{\circ} \mathrm{C}$ and constant pressure $\mathrm{cal}^{\circ} \mathrm{C}^{-1} \mathrm{~mol}^{-1}$
$P_{c}$ Critical pressure in atm
$V_{\mathrm{c}}$ Critical volume in $\mathrm{ml} \mathrm{mol}^{-1}$
$T_{\text {c }}$ Critical temperature in ${ }^{\circ} \mathrm{C}$
$R_{\mathrm{m}}$ Molar refractivity at $25^{\circ} \mathrm{C}$ in $\mathrm{ml} \mathrm{mol}^{-1}$
$R_{\mathrm{i}}$ Intercept refractivity
$T_{v}$ Vapor pressure at $25^{\circ} \mathrm{C}$ in mmHg
$M_{\mathrm{w}}$ Molecular weight in g
$Y_{i} \quad$ Properties
$X_{\mathrm{i}}$ Contribution of component $i$ to mixture of petroleum fractions
$\nu$ Kinematic viscosity

## 1. INTRODUCTION

The increasing interest in crude oil when it was new material in the chemical industry led to thorough studies of its composition and properties. Crude oil and its product derivatives are quite complex blends of hydrocarbons that each contribute by their nature and their concentration to the unknown physical properties of the blend.

We have to note that some of these physical properties, such as the critical and thermal ones, are difficult and costly to obtain experimentally. In such a case, one will have to resort to the use of either empirical equations or graphics. The purpose of our work has been a thorough study of the physicochemical properties and the composition of petroleum fractions. Hence, we attempted to approach the thermodynamical properties of pure components and petroleum fractions by proposing empirical equations and correlations found by using different mixture rules. These properties have been worked out for light hydrocarbons for temperatures varying from $10^{\circ} \mathrm{C}$ to $180^{\circ} \mathrm{C}$.

## 2. EQUATIONS RELATING PHYSICOCHEMICAL PROPERTIES

### 2.1. Newton's Polynomial Interpolation Method

Using the interpolation method of the Newton polynomial and with the help of the computer, we obtained equations that relate the physical and chemical properties of the five families considered: paraffins, isoparaffins, olefines, naphthenes, and aromatics. Knowing one physical or chemical property, it is possible to get, from these equations, the other unknown ones. The equations are of the form: $y=f\left(x^{5}, x^{4}, x^{3}, x^{2}, x^{1}, x^{0}\right)$.

In Table 1, the coefficients for the relationships between the boiling temperature and the other properties are given for the paraffin family. For instance, the critical pressure reads from Table 1 as:

$$
\begin{align*}
P_{\mathrm{c}}= & -8.53 \times 10^{-10} T_{\mathrm{b}}^{5}+4.527 \times 10^{-7} T_{\mathrm{b}}^{4} \\
& -9.341 \times 10^{-5} T_{\mathrm{b}}^{3}+9.141 \times 10^{-3} T_{\mathrm{b}}^{2} \\
& -0.527 T_{\mathrm{b}}+43.830 . \tag{1}
\end{align*}
$$

Fifteen other tables similar to Table 1 have been developed to show any property as a function of any other specific one.
In those tables $T_{\mathrm{b}}^{5}, \ldots T_{\mathrm{b}}^{\mathrm{o}}$ are replaced by $P_{\mathrm{c}}^{5}, \ldots P_{\mathrm{c}}^{\mathrm{o}}$, or by $T_{\mathrm{c}}^{\mathrm{s}}, \ldots T_{\mathrm{c}}^{\mathrm{o}}$, and so on.

Furthermore, sixteen tables of the same type are also available for each of the other four families: naphthenes, aromatics, isoparaffins, and olefines.

We wish to point out that this method has been very useful, especially when it was not easy to assess some properties experimentally.

### 2.2. Equations of the Form $\boldsymbol{Y}_{i}=A M_{w}+B T_{b}+C$

We propose an equation of the form:

$$
\begin{equation*}
Y_{i}=A M_{\mathrm{w}}+B T_{\mathrm{b}}+C . \tag{2}
\end{equation*}
$$

The equation requires two parameters, the molecular weight and the boiling point, in order to obtain other properties for paraffins, naphthenes, and aromatics. The coefficients $A, B$, and $C$ are given in Table 2.

Table 1. Coefficients for the Properties of Paraffins Using Equation (1)

|  | $T_{\mathrm{b}}^{5}$ | $T_{\mathrm{b}}^{4}$ | $T_{\mathrm{b}}^{3}$ | $T_{\mathrm{b}}^{2}$ | $T_{\mathrm{b}}^{1}$ | $T_{\mathrm{b}}^{\mathrm{o}}$ |
| :--- | :--- | :---: | :--- | :--- | :--- | :--- | :--- |
| $P_{\mathrm{c}}$ | $-8.533 \times 10^{-10}$ | $+4.572 \times 10^{-7}$ | $-9.341 \times 10^{-5}$ | $+9.141 \times 10^{-3}$ | -0.521 | +43.830 |
| $T_{\mathrm{c}}$ | $-9.778 \times 10^{-10}$ | $+5.122 \times 10^{-7}$ | $-10.016 \times 10^{-5}$ | $+8.230 \times 10^{-3}$ | +0.867 | +158.425 |
| $V_{\mathrm{c}}$ | $+5.833 \times 10^{-9}$ | $-3.107 \times 10^{-6}$ | $+62.776 \times 10^{-5}$ | $-58.066 \times 10^{-3}$ | +4.465 | +193.936 |
| $d$ | $-3.041 \times 10^{-13}$ | $-1.338 \times 10^{-10}$ | $-1.396 \times 10^{-8}$ | $-3.026 \times 10^{-6}$ | $+13.880 \times 10^{-4}$ | +0.575 |
| $n$ | $-5.872 \times 10^{-14}$ | $+8.238 \times 10^{-12}$ | $+7.281 \times 10^{-9}$ | $-3.198 \times 10^{-6}$ | $-8.076 \times 10^{-4}$ | +1.330 |
| $T_{\mathrm{v}}$ | $-2.089 \times 10^{-8}$ | $+1.480 \times 10^{-5}$ | $-42.869 \times 10^{-4}$ | $+64.132 \times 10^{-2}$ | -50.215 | +1666.576 |
| $H_{\mathrm{v}}$ | $+3.760 \times 10^{-10}$ | $-2.041 \times 10^{-7}$ | $+4.130 \times 10^{-5}$ | $-3.620 \times 10^{-3}$ | $-23.600 \times 10^{-3}$ | +84.324 |
| $C_{\mathrm{g}}$ | $+1.243 \times 10^{-7}$ | $-6.717 \times 10^{-5}$ | $+13.784 \times 10^{-3}$ | -1.328 | +59.815 | -827 |
| $C_{\mathrm{p}}$ | $+7.750 \times 10^{-11}$ | $-4.103 \times 10^{-8}$ | $+8.490 \times 10^{-6}$ | $-55.115 \times 10^{-5}$ | +0.174 | +22.830 |
| $H_{\mathrm{c}}$ | $+1.620 \times 10^{-9}$ | $-8.900 \times 10^{-7}$ | $+19.402 \times 10^{-5}$ | -0.012 | +4.900 | +670.364 |
| $R_{\mathrm{m}}$ | $+2.250 \times 10^{-11}$ | $-1.340 \times 10^{-8}$ | $+3.267 \times 10^{-6}$ | $-13.833 \times 10^{-5}$ | +0.136 | +20.427 |
| $V_{\mathrm{A}}$ | $-1.560 \times 10^{-11}$ | $+8.936 \times 10^{-9}$ | $+1.828 \times 10^{-6}$ | $+18.700 \times 10^{-5}$ | $-67.327 \times 10^{-4}$ | +0.300 |
| $T_{\mathrm{s}}$ | $-1.011 \times 10^{-10}$ | $+5.500 \times 10^{-8}$ | $-1.114 \times 10^{-5}$ | $+8.830 \times 10^{-4}$ | $-46.200 \times 10^{-3}$ | +13.102 |
| $R_{\mathrm{i}}$ | $-1.925 \times 10^{-14}$ | $+5.753 \times 10^{-12}$ | $+2.045 \times 10^{-10}$ | $-2.411 \times 10^{-7}$ | $+4.525 \times 10^{-5}$ | +1.042 |
| $M_{\mathrm{w}}$ | $+1.157 \times 10^{-10}$ | $-6.373 \times 10^{-8}$ | $+1.413 \times 10^{-5}$ | $-78.259 \times 10^{-5}$ | +0.426 | +57.232 |

Table 2. Coefficients for the Properties of Paraffins Valid in the Temperature Range $35-175^{\circ} \mathrm{C}$

|  | $A$ | $B$ | $C$ |
| :--- | :--- | :--- | :--- |
| $P_{\mathrm{c}}$ | -0.0925 | -0.04557 | +40.8337 |
| $T_{\mathrm{c}}$ | +1.0940 | +0.5390 | +102.9808 |
| $V_{\mathrm{c}}$ | +2.1744 | +1.0713 | +108.9875 |
| $d$ | $+7.785 \times 10^{-4}$ | $+3.835 \times 10^{-4}$ | +0.5613 |
| $n$ | $+4.062 \times 10^{-4}$ | $+2.001 \times 10^{-4}$ | +1.3235 |
| $H_{v}$ | -0.1429 | -0.0704 | +97.1884 |
| $C_{\mathrm{g}}$ | +0.6871 | +0.3385 | +95.3299 |
| $C_{\mathrm{p}}$ | +0.195 | $+9.606 \times 10^{-2}$ | +10.7945 |
| $H_{\mathrm{c}}$ | +5.57 | +2.744 | +326.3902 |
| $R_{\mathrm{m}}$ | +0.1654 | $+8.149 \times 10^{-2}$ | +10.0718 |
| $T_{\mathrm{s}}$ | $+5.989 \times 10^{-2}$ | $+2.95 \times 10$ | +10.7115 |
| $R_{\mathrm{i}}$ | $+1.675 \times 10^{-5}$ | $+0.825 \times 10^{-5}$ | +1.04285 |

Table 3. Coefficients for the Properties of Naphthenes Valid in the Temperature Range $50-185^{\circ} \mathrm{C}$

|  | $A$ | $B$ | $C$ |
| :--- | :--- | :--- | :--- |
| $P_{\mathrm{c}}$ | -0.1485 | -0.0822 | +59.3355 |
| $T_{\mathrm{c}}$ | +1.0171 | +0.563 | +149.3604 |
| $V_{\mathrm{c}}$ | +2.008 | +1.1114 | +49.2886 |
| $n$ | $+1.336 \times 10^{-4}$ | $+0.739 \times 10^{-4}$ | +1.4063 |
| $d$ | $+1.887 \times 10^{-4}$ | $+1.044 \times 10^{-4}$ | +0.7496 |
| $H_{\mathrm{v}}$ | -0.1994 | -0.1104 | +110.7674 |
| $C_{\mathrm{p}}$ | +0.2214 | +0.1225 | -3.1195 |
| $H_{\mathrm{c}}$ | +5.5189 | +3.0546 | +228.8171 |
| $R_{\mathrm{m}}$ | +0.166 | +0.0919 | +6.3393 |
| $T_{\mathrm{s}}$ | $+1.747 \times 10^{-2}$ | $+9.66 \times 10^{-3}$ | +22.1297 |
| $R_{\mathrm{i}}$ | $+3.921 \times 10^{-5}$ | $+2.17 \times 10^{-5}$ | +1.0315 |

Table 4. Coefficients for the Properties of Aromatics
Valid in the Temperature Range $80-185^{\circ} \mathrm{C}$

|  | $A$ | $B$ | $C$ |
| :--- | :--- | :--- | :--- |
| $P_{\mathrm{c}}$ | -0.1991 | -0.1059 | +72.3759 |
| $T_{\mathrm{c}}$ | +0.9056 | +0.4815 | +179.7013 |
| $V_{\mathrm{c}}$ | +2.1506 | +1.1434 | -1.1518 |
| $d$ | $-1.889 \times 10^{-4}$ | $-1.005 \times 10^{-4}$ | +0.8965 |
| $n$ | $-9.993 \times 10^{-5}$ | $-5.313 \times 10^{-5}$ | +1.510 |
| $H_{\mathrm{v}}$ | -0.2154 | -0.1145 | +120.1306 |
| $C_{\mathrm{p}}$ | +0.2007 | +0.1067 | +112.3784 |
| $H_{\mathrm{c}}$ | +5.5394 | +2.9452 | +112.3784 |
| $T_{\mathrm{s}}$ | $+3.208 \times 10^{-3}$ | $+1.706 \times 10^{-3}$ | +27.7928 |
| $R_{\mathrm{i}}$ | $-0.5466 \times 10^{-5}$ | $-2.906 \times 10^{-6}$ | +1.0617 |

Table 5. Coefficients for the Properties of Isoparaffins Valid in the Temperature Range $28-145^{\circ} \mathrm{C}$

|  | $A$ | $B$ | $C$ |
| :--- | :--- | :--- | :--- |
| $P_{\mathrm{c}}$ | $-9.267 \times 10^{-2}$ | $-4.538 \times 10^{-2}$ | +40.4275 |
| $T_{\mathrm{c}}$ | +1.1068 | +0.5419 | +96.3889 |
| $V_{\mathrm{c}}$ | +2.1566 | +1.0558 | +117.3793 |
| $d$ | $+8.02 \times 10^{-4}$ | $+3.927 \times 10^{-4}$ | +0.5562 |
| $n$ | $+4.349 \times 10^{-4}$ | $+2.129 \times 10^{-4}$ | +1.3192 |
| $H_{\mathrm{v}}$ | -0.1175 | $-5.7504 \times 10^{-2}$ | +90.485 |
| $C_{\mathrm{p}}$ | +0.1943 | $+9.5113 \times 10^{-2}$ | +11.4835 |
| $H_{\mathrm{c}}$ | +5.5709 | +2.7275 | +348.8839 |
| $R_{\mathrm{m}}$ | +0.1646 | $+8.059 \times 10^{-2}$ | +10.8543 |

## 3. APPLICATION OF THE EQUATIONS USING "NEWTON INTERPOLATION" TO DIFFERENT MIXTURES

### 3.1. Application to Mixtures of Pure Components of the Same Family

A comparison of experimental and estimated properties is given in Table 6 for a mixture of three paraffinic pure components, pentane, hexane, and heptane in equivolumetric proportion.

Apart from the viscosity, all the properties are calculated by using the additivity rules according to the following equation:

$$
\begin{equation*}
Y=\frac{\sum Y_{i} X_{i}}{\sum X_{i}} \tag{3}
\end{equation*}
$$

where $Y$ is the mixture property; $Y_{i}$ is the property of component $i$; and $X_{i}$ is the mole fraction of component $i$.

The kinematic viscosity $v$ is not an additive property. Hence we have to apply the following relationship:

$$
\begin{equation*}
\ln v=\frac{\Sigma X_{i} \ln \nu_{i}}{\Sigma X_{i}} ; \text { with } \quad v=\frac{V_{\mathrm{A}}}{d}, \tag{4}
\end{equation*}
$$

where $V_{\mathrm{A}}$ is the absolute viscosity and $d$ is the density, both measured at the same temperature.

The deviations between experimental and estimated values have been of the same acceptable order as shown in Table 6 for a multitude of other mixtures and properties. Hence this method may be used reliably in estimating properties of mixtures of components of the same family.

### 3.2. Application to Mixtures of Pure Components from Different Families

In order to estimate the validity of these equations, several mixtures of hydrocarbons containing different families have been studied. In Table 7, we

Table 6. Comparison of Calculated and Experimental Values of Refractive Index, Density, and Kinematic Viscosity for Pure Component Mixtures

| Property | $n^{20}$ | $d^{20}\left(\mathrm{~g} \mathrm{ml}^{-1}\right)$ | $\nu$ (centistokes) |
| :--- | :--- | :--- | :---: |
| Calculated <br> value | 1.36947 | 0.64955 | 0.488 |
| Experimental <br> value | 1.3720 | 0.64955 | 0.435 |
| Deviation \% | 0.18 | 0.00 | 2.98 |

give only the results for a pure $\mathrm{C}_{8}$ component mixture of members of the following families:
n -paraffins (n-octane); naphthenes (cyclo-octane); aromatics (ethylbenzene); isoparaffins (isooctane).

For each property, an equimolar mixture is represented in column 1 and an equivolumetric mixture is represented in column 2. The good agreement between experimental and estimated values as shown in Table 7 shows the Newton type of equations to be valid also for mixtures of pure components from different families.

Furthermore, we can say that the hypothesis of additivity is reasonable.

### 3.3. Application to Petroleum Fractions

Knowing the composition of a petroleum fraction and one of its properties (obtained experimentally), all the other properties are computed using the equations derived from the Newton interpolation and using as above the additivity rule. Below, only two petroleum fractions of the several considered are used as examples. In these two cases the composition and the boiling point are the two known parameters.

1. Fraction 9 taken from the distillation of HassiMessouad crude oil (Algeria) [1] with a boiling temperature $T_{\mathrm{b}}=115^{\circ} \mathrm{C}$ and paraffin, naphthenes, and aromatic contributions found by gas chromatography being respectively $X_{\mathrm{p}}=54.7 \%$, $X_{\mathrm{n}}=42.1 \%, X_{\mathrm{a}}=3.3 \%$ (see Table 8).

Table 7. Comparison of Calculated and Experimental Values of Mixture Properties of Pure Components From Different Families

| Property | $n$ |  | $d\left(\mathrm{~g} \mathrm{ml}^{-1}\right)$ |  | $\nu$ (centistokes) |  | $T_{\mathrm{b}}\left({ }^{\circ} \mathrm{C}\right)$ |  | $T_{\mathrm{s}}\left(\mathrm{dyn} \mathrm{cm}^{-1}\right)$ |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 1 | 2 | 1 | 2 | 1 | 2 | 1 | 2 | 1 | 2 |
| Calculated value | 1.42822 | 1.43314 | 0.7597 | 0.7682 | 0.7818 | 0.7846 | 127.8 | 128.6 | 23.8 | 24.19 |
| Experimental value | 1.42812 | 1.43411 | 0.7594 | 0.7710 | 0.7713 | 0.7806 | 127.1 | 129.4 | 24.0 | 24.4 |
| Deviation \% | 0.07 | 0.068 | 0.04 | 0.36 | 1.3 | 0.5 | 0.55 | 0.6 | 0.84 | 0.87 |

2. Fraction 30 taken from the distillation of HassiMessaoud crude oil [1] with the following characteristics: $T_{\mathrm{b}}=175^{\circ} \mathrm{C}$, and from gas chromatography; $X_{\mathrm{p}}=57.1 \%, X_{\mathrm{n}}=0 \%, X_{\mathrm{a}}=42.9 \%$ (see Table 9).
We can notice from Tables 8 and 9 that the equations derived from the Newton interpolations may be applied for petroleum fractions as well.

## 4. APPLICATION OF EQUATIONS OF THE FORM $Y_{i}=A M_{w}+B T_{b}+C$

The application of the equations of the form $Y_{i}=A M_{\mathrm{w}}+B T_{\mathrm{b}}+C$ has been carried out for dif-
ferent components, different mixtures of components and different petroleum fractions. The results are given for pure compounds in Table 10; for mixtures of pure compounds in Table 11; and for petroleum fractions in Table 12.

For pure components, the differences between our estimated values and those given in reference [2] are less than $5 \%$.

The results in Table 11 are for a mixture of four pure $\mathrm{C}_{8}$ components from the n-paraffin, naphthene, and aromatic families. Column 1 represents an equimolar mixture with $T_{\mathrm{b}}=127.05^{\circ} \mathrm{C}$ and $M_{\mathrm{w}}=113 \mathrm{~g}$;

Table 8. Comparison of Calculated and Experimental Values of Properties of Fraction 9 of Hassi-Messouad Crude Oil

| Property | $P_{\mathrm{c}}$ | $T_{\mathrm{c}}$ | $V_{\mathrm{c}}$ | $d$ | $M_{\mathrm{w}}$ | $H_{\mathrm{v}}$ | $T_{\mathrm{s}}$ | $R_{\mathrm{i}}$ | $n$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| Experimental value | 28.02 | 299.4 | 431.0 | 0.740 | 110.6 | 72.92 | 20.32 | 1.041 | 1.411 |
| Calculated value | 28.06 | 295.6 | 437.7 | 0.734 | 108.8 | 73.23 | 22.24 | 1.043 | 1.409 |
| Deviation \% | 0.10 | 1.10 | 1.50 | 0.80 | 1.60 | 0.40 | 9.4 | 0.24 | 0.1 |

Table 9. Comparison of Calculated and Experimental Values of Properties of Fraction 30 of Hassi-Messouad Crude Oil

| Property | $P_{\mathrm{c}}$ <br> $(\mathrm{atm})$ | $T_{\mathrm{c}}$ <br> $\left({ }^{\circ} \mathrm{C}\right)$ | $M_{\mathrm{w}}$ <br> $(\mathrm{g})$ | $R_{\mathrm{i}}$ | $T_{\mathrm{s}}$ <br> $\left(\mathrm{dyncm}^{-1}\right)$ | $R_{\mathrm{m}}$ <br> $\left(\mathrm{ml} \mathrm{mol}^{-1}\right)$ | $H_{\mathrm{c}}$ <br> $\left(\mathrm{kcal} \mathrm{mol}^{-1}\right)$ | $C_{\mathrm{p}}$ <br> $\left(\mathrm{cal} \mathrm{mol}^{-1}\right)$ | $C_{\mathrm{g}}$ <br> $\left({ }^{\circ} \mathrm{C}\right)$ |
| :--- | :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Experimental value | 24.7 | 356 | 137 | 1.0561 | 24.7 | 46.25 | 1520.7 | 49.7 | -56 |
| Calculated value | 24.35 | 364.7 | 137.16 | 1.0522 | 25.67 | 46.52 | 1491.2 | 18.34 | -57 |
| Deviation \% | 14 | 2.4 | 0.1 | 0.2 | 4.9 | 0.6 | 1.9 | 1.8 | 2.0 |

Table 10. Comparison of the Properties of $\mathbf{C}_{7}$ Pure Components in Each Family.

| Property | Isoparaffin: isoheptane |  | n -Paraffin: <br> n-heptane |  | Naphthene: methylcyclohexane |  | Aromatics: toluene |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Values | Calculated* | A. P. I. <br> [2] | Calcu- <br> lated* | A. P. I. <br> [2] | Calcu- <br> lated* | A. P. I. [2] | Calculated* | A. P. I. <br> [2] |
| $P_{c}(\mathrm{~atm})$ | 27.05 | 27 | 27.08 | 27 | 36.45 | 34.26 | 42.31 | 40.55 |
| $T_{\mathrm{c}}\left({ }^{\circ} \mathrm{C}\right)$ | 256.1 | 257.3 | 265.7 | 267.1 | 306.1 | 299.0 | 316.4 | 318.6 |
| $V_{\mathrm{c}}\left(\mathrm{ml} \mathrm{mol}^{-1}\right)$ | 428.6 | 421.0 | 432.4 | 432.0 | 358.6 | 368.0 | 323.4 | 316.0 |
| $d\left(\mathrm{~g} \mathrm{ml}^{-1}\right)$ | 0.6719 | 0.675 | 0.6771 | 0.6795 | 0.7786 | 0.7650 | 0.868 | 0.8623 |
| $n$ | 1.3819 | 1.3829 | 1.38391 | 1.38511 | 1.94269 | 1.42058 | 1.4949 | 1.49413 |
| $H_{\mathrm{v}}\left(\mathrm{cal} \mathrm{g}^{-1}\right)$ | 73.53 | 73.40 | 75.93 | 75.61 | 80.05 | 75.58 | 87.61 | 86.08 |
| $C_{\mathrm{g}}(\mathrm{K})$ | - | - | 197.5 | 182.6 | - | - | - | - |
| $C_{\mathrm{p}}\left(\mathrm{cal}^{\circ} \mathrm{C}^{-1} \mathrm{~mol}^{-1}\right)$ | 39.52 | 39.42 | 39.79 | 39.67 | 30.98 | 32.27 | 25.59 | 24.8 |
| $H_{\mathrm{c}}\left(\mathrm{kcal} \mathrm{mol}^{-1}\right)$ | 1152.8 | 1149.9 | 1154.8 | 1151.3 | 1076.8 | 1091.1 | 948.6 | 934.5 |
| $R_{\mathrm{m}}\left(\mathrm{ml} \mathrm{mol}^{-1}\right)$ | 34.6 | 34.5 | 34.7 | 34.6 | 31.9 | 32.5 | - | - |
| $T_{\mathrm{s}}\left(\right.$ dyn cm $\left.^{-1}\right)$ | - | - | 19.6 | 19.8 | 24.8 | 23.2 | 28.3 | 27.9 |
| $R^{\text {i }}$ | - | - | 1.04530 | 1.04536 | 1.0376 | 1.03805 | 1.0609 | 1.06298 |

${ }^{*}$ Using $Y_{i}=A M_{\mathrm{w}}+B T_{\mathrm{b}}+C$

Table 11. Comparison of the Properties of Pure Component Mixtures

|  | $n$ |  |  | $d\left(\mathrm{~g} \mathrm{ml}^{-1}\right)$ |  |
| :--- | :---: | :---: | :--- | :--- | :--- |
| Property | 1 |  | 2 |  | 1 |
| Experimental <br> value | 1.42818 | 1.43411 |  | 0.75935 | 0.7710 |
| Calculated <br> value | 1.42796 | 1.43685 | 0.7596 | 0.7603 |  |
| Deviation $\%$ | 0.015 | 0.19 |  | 0.03 | 0.14 |

column 2 represents an equivolumetric mixture with $T_{\mathrm{b}}=129.4^{\circ} \mathrm{C}$ and $M_{\mathrm{w}}=111.7 \mathrm{~g}$.

Fraction 5 taken from the distillation of Guellala crude oil (Algeria) [1] has the following composition: $\quad X_{\mathrm{p}}=70.6 \%, \quad X_{\mathrm{n}}=29.4 \%, \quad X_{\mathrm{a}}=0 \%$. The boiling temperature and molecular weight are: $T_{\mathrm{b}}=76^{\circ} \mathrm{C}$ and $M_{\mathrm{w}}=90.8 \mathrm{~g}$. The calculated and experimental values of its properties are compared in Table 12.

Fraction 30 taken from the distillation of HassiMessaoud crude oil [1] has the following composition: $X_{\mathrm{p}}=57.1 \%, X_{\mathrm{n}}=0 \%, X_{\mathrm{a}}=42.9 \%$, and it is known that $T_{\mathrm{b}}=175^{\circ} \mathrm{C}$ and $M_{\mathrm{w}}=137 \mathrm{~g}$. The calculated and experimental values of the properties of this fraction are compared in Table 13.

We can notice that equations of the form $Y_{i}=A M_{\mathrm{w}}+B T_{\mathrm{b}}+C$ give an estimation of properties of pure components, mixtures of pure components, and light petroleum fractions in good agreement with those obtained experimentally.

However, the discrepancy is slightly larger, though still within acceptable limits, for a fraction which has a quite high composition of aromatics.

## 5. PROPOSED CORRELATIONS FOR FINDING THE COMPOSITION OF DIFFERENT FRACTIONS

To predict the physical and thermodynamical properties of petroleum fractions, we need to find the proportion of paraffinic, naphthenic, and aromatic hydrocarbons which are present in the fraction. Several well-known methods such as gaseous phase chromatography (GPC) refractive index density aniline point (ndPA) [3], and Riazi-Daubert [4], have been developed to derive the proportions, which are not easy to find experimentally.

In the following, we propose two correlations that help in getting the composition of light petroleum fractions in the temperature range between 10 and $180^{\circ} \mathrm{C}$.

We start with a system of three equations with three unknowns. One of the equations is:

$$
\begin{equation*}
X_{\mathrm{p}}+X_{\mathrm{n}}+X_{\mathrm{a}}=1 \tag{5}
\end{equation*}
$$

The two other equations are put in the following form:

$$
\begin{gather*}
a X_{\mathrm{p}}+b X_{\mathrm{n}}+c X_{\mathrm{a}}=A  \tag{6}\\
a^{\prime} X_{\mathrm{p}}+b^{\prime} X_{\mathrm{n}}+c^{\prime} X_{\mathrm{a}}=B \tag{7}
\end{gather*}
$$

The parameters $A$ and $B$ are chosen such that when they are applied to the five hydrocarbons of

Table 12. Comparison of Calculated and Experimental Values of Properties of Fraction 5 of Guellala Crude Oil

| Property | $\begin{gathered} P_{c} \\ (\mathrm{~atm}) \end{gathered}$ | $\begin{gathered} T_{\mathrm{c}} \\ \left({ }^{\circ} \mathrm{C}\right) \end{gathered}$ | $\begin{gathered} V_{\mathrm{c}} \\ \left(\mathrm{ml} \mathrm{~mol}^{-1}\right) \end{gathered}$ | $\begin{gathered} C_{\mathrm{p}} \\ \left(\operatorname{cal}^{\circ} \mathrm{C}^{-1}\right) \end{gathered}$ | $\begin{gathered} H_{\mathrm{v}} \\ \left(\mathrm{cal} \mathrm{~g}^{-1}\right) \end{gathered}$ | $n$ | $\begin{gathered} R_{\mathrm{m}} \\ \left(\mathrm{ml} \mathrm{~mol}^{-1}\right) \end{gathered}$ | $R_{\text {i }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Experimental value | 31.7 | 249.6 | 371 | 33.14 | 77.92 | 1.3890 | 30.98 | 1.0425 |
| Calculated value | 32.1 | 255.1 | 366.7 | 33.01 | 80.49 | 1.3898 | 30.43 | 1.04258 |
| Deviation \% | 1.3 | 2.2 | 1.2 | 0.4 | 3.3 | 0.06 | 1.8 | 0.008 |

Table 13. Comparison of Calculated and Experimental Values of Properties of Fraction 30 of Hassi-Messouad Crude Oil.

| Property | $P_{\mathrm{c}}$ <br> $(\mathrm{atm})$ | $T_{\mathrm{c}}$ <br> $\left({ }^{\circ} \mathrm{C}\right)$ | $C_{\mathrm{p}}$ <br> $\left(\mathrm{cal}^{\circ} \mathrm{C}^{-1} \mathrm{~mol}^{-1}\right)$ | $H_{\mathrm{c}}$ <br> $\left(\mathrm{kcal} \mathrm{mol}^{-1}\right)$ | $T_{\mathrm{s}}$ <br> $\left(\mathrm{dyn} \mathrm{cm}^{-1}\right)$ | $R_{\mathrm{i}}$ |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: |
| Experimental value | 24.7 | 356 | 49.7 | 1520.7 | 24.7 | 1.0501 |
| Calculated value | 22.9 | 364.7 | 48.8 | 1491.2 | 25.9 | 1.0525 |
| Deviation \% | 7.3 | 2.4 | 1.8 | 1.9 | 4.9 | 0.2 |

each family and when they are plotted versus the temperature, we get curves that do not cross each other in the interval of temperature considered. The coefficients $a, b, c$ are respectively the mean values of $A$ for the paraffin, naphthene, and aromatic components. The coefficients $a^{\prime}, b^{\prime}, c^{\prime}$ are respectively the mean values of $B$ for the paraffin, naphthene, and aromatic components.

For the purpose of finding the correlations we use five identical hydrocarbons from each family ( $\mathrm{C}_{6}$, $\mathrm{C}_{7}, \mathrm{C}_{8}, \mathrm{C}_{9}$, and $\mathrm{C}_{10}$ for the paraffins, naphthenes, and aromatics) with their properties as given in A.P.I. [2].

## Correlation 1

Based on knowing the density, the molecular weight, and the refractive index:

$$
\begin{gather*}
X_{\mathrm{p}}=6244.549 A+2.854 \times 10^{-4} B+71.4647  \tag{8}\\
X_{\mathrm{n}}=7793.582 A-7.072 \times 10^{-4} B-0.2973  \tag{9}\\
X_{\mathrm{a}}=1549.033 A+4.219 \times 10^{-4} B-0.1673  \tag{10}\\
\text { Let } A=d^{7.3} / M^{1.26}  \tag{11}\\
B=n^{22} \tag{12}
\end{gather*}
$$

## Correlation 2

Knowing the density, the refractive index, and the boiling temperature, then in this case:
and

$$
\begin{equation*}
A=4 T_{\mathrm{b}} /(d n)^{30} \tag{13}
\end{equation*}
$$

$$
\begin{equation*}
B=n^{16.8} \tag{14}
\end{equation*}
$$

Table 14 (overleaf) summarizes the results of our two correlations and those obtained through the use of GPC, ndPA, and Riazi-Daubert, when applied to the first seventeen petroleum fractions taken from the distillation of Hassi-Messaoud crude oil [1].
One can see that our results compare favorably with those of other correlations.

## 6. CONCLUSIONS

First, the equations of the "Newton polynomial" type helped us to derive all the physical properties, if
only one property is known. On the other hand, equations of the type $Y_{i}=A M_{\mathrm{w}}+B T_{\mathrm{b}}+C$ need two known properties in order to find the rest. However, these two properties, the boiling point and the molecular weight, are very easily obtained experimentally. The results of these two types of equations are very satisfactory.

Secondly, the two correlations that we are proposing give the compositions of petroleum fractions that compare quite well with the compositions given by other methods. The characteristics needed for our correlations are the density, the refractive index, and the boiling point or the molecular weight. As these are easily obtained experimentally, our correlations can be more useful than some other methods.

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Table 14. Comparison of Paraffin, Naphthene, and Aromatic Fractions in
Hassi-Messaoud Crude Oil Obtained from Experiments and Correlation Methods.

| Fraction | $X_{\text {p }}$ \% |  |  |  |  | $X_{\mathrm{n}}$ \% |  |  |  |  | $X_{\text {a }}$ \% |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | GPC | ndPA | RiaziDaubert | Correlation 2 | Correlation 1 | GPC | ndPA | RiaziDaubert | Correlation 2 | Correlation 1 | GPC | ndPA | RiaziDaubert | Correlation 2 | Correlation 1 |
| 01 | 100 | - | - | - | 93.81 | 0 | - | - | - | 5.05 | 0 | - | - | - | 1.12 |
| 02 | 85.72 | - | - | - | 84.80 | 12.08 | - | - | - | 12.04 | 2.20 | - | - | - | 3.14 |
| 03 | 73.33 | - | 89.55 | 81.04 | 78.41 | 15.00 | - | 3.60 | 17.45 | 16.47 | 3.34 | - | 6.85 | 1.50 | 5.11 |
| 04 | 71.26 | 66.35 | 83.95 | 77.60 | 70.90 | 18.10 | 19.60 | 8.00 | 18.25 | 21.26 | 10.64 | 14.05 | 7.96 | 4.14 | 7.82 |
| 05 | 70.63 | 68.69 | 68.05 | 65.20 | 56.88 | 29.37 | 23.08 | 27.44 | 29.92 | 34.42 | 0 | 8.23 | 4.51 | 4.87 | 8.68 |
| 06 | 70.56 | 66.30 | 66.28 | 54.87 | 43.55 | 29.44 | 22.47 | 24.62 | 35.39 | 42.03 | 0 | 11.23 | 9.10 | 9.73 | 14.41 |
| 07 | 63.78 | 64.94 | 59.66 | 46.83 | 35.78 | 28.29 | 24.43 | 30.98 | 40.62 | 46.13 | 7.93 | 10.53 | 9.36 | 12.53 | 18.07 |
| 08 | 58.33 | 64.83 | 55.72 | 44.70 | 32.14 | 41.67 | 25.05 | 34.52 | 39.94 | 46.65 | 0 | 10.12 | 9.76 | 15.34 | 21.19 |
| 09 | 54.68 | 63.75 | 55.05 | 46.41 | 34.08 | 42.10 | 25.65 | 34.90 | 35.30 | 41.06 | 3.22 | 10.60 | 10.05 | 18.28 | 24.85 |
| 10 | 58.23 | 63.55 | 59.50 | 45.61 | 32.03 | 26.22 | 21.92 | 24.69 | 28.62 | 34.42 | 15.55 | 14.53 | 15.81 | 25.76 | 33.53 |
| 11 | 90.43 | - | 76.74 | 28.32 | 37.64 | 9.57 | - | 14.79 | 49.39 | 36.61 | 0 | - | 8.47 | 22.28 | 25.73 |
| 12 | 77.26 | - | 70.83 | 53.51 | 40.06 | 22.74 | - | 20.74 | 8.70 | 26.80 | 0 | - | 8.43 | 37.78 | 33.12 |
| 13 | 64.65 | - | 66.83 | 27.62 | 31.97 | 35.35 | - | 24.28 | 40.17 | 32.02 | 0 | - | 8.84 | 32.20 | 35.99 |
| 14 | 59.20 | 66.29 | 64.92 | 25.99 | 30.85 | 21.26 | 22.43 | 25.41 | 39.28 | 26.91 | 19.54 | 11.28 | 9.67 | 34.71 | 42.23 |
| 15 | - | 58.7 | - | 25.32 | 28.28 | - | 34.8 | - | 35.92 | 20.16 | - | 6.5 | - | 38.74 | 51.55 |
| 16 | - | 52.6 | - | 27.25 | 33.24 | - | 35.5 | - | 30.89 | 9.38 | - | 11.9 | - | 41.85 | 53.37 |
| 17 | - | 58.4 | - | 17.17 | 36.13 | - | 30.2 | - | 35.27 | 0.97 | - | 11.4 | - | 47.55 | 62.89 |


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