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A New Characterization Factor for Hydrocarbons and Petroleum Fluids Fractions

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Résumé — **Un nouveau facteur de caractérisation pour les hydrocarbures et les fractions fluides de pétrole** — Sur la base de l'équation bien connue de Lorentz-Lorenz et de la nature additive du paramètre de réfraction molaire, les auteurs proposent ici un nouveau facteur de caractérisation en tant que fonction d'indice de réfraction et de densité pour les hydrocarbures purs et les fractions de pétrole. Ce facteur spécifie chaque fraction d'hydrocarbure et de pétrole, en particulier par rapport à d'autres facteurs de caractérisation. Il permet de délimiter avec précision les plages de valeurs correspondant aux différentes séries homologues d'hydrocarbures, telles les séries paraffiniques, naphténiques et aromatiques, sans chevauchement entre plages apparentées. Par ailleurs, on propose, pour ce paramètre, une règle de mélange reposant sur une base théorique, alors que pour les autres facteurs de caractérisation, on applique la règle de Kay, qui n'en possède aucune.

Abstract *— **A New Characterization Factor For Hydrocarbons and Petroleum Fluids Fractions** — Using the well-known equation of Lorentz-Lorenz and the additivity nature of the molar refraction parameter, a new characterization factor as a function of the refractive index and density is proposed for pure hydrocarbons and petroleum fractions, which uniquely specifies every hydrocarbon and oil fraction in comparison with other characterization factors. This factor can separate, precisely, the range of the values of the various hydrocarbon homologue series such as paraffins, naphthenes, and aromatics from one another without any overlap between related ranges. On the other hand a mixing rule for this parameter is presented, which has a theoretical basis whereas in the other characterization factors Kay's rule is applied, which has no theoretical basis.*

NOTATIONS

d Density
I Refractive index parameter
K_W Watson characterization factor
M Molecular weight
n Sodium D-line refractive index of liquid at 20°C and 1 atm
N Carbon number
N_A Avogadro's number
R Molar refraction
RI Refractivity intercept
S Specific gravity
T_b Boiling point
V_i Molar volume of component i
VGC Viscosity gravity constant.

Greek Letters

α Distortion polarizability
φ_i Volume fraction of component i
π 3.14159.

INTRODUCTION

Since the exact identification of all the components of such complex mixtures as petroleum fluids and coal liquids, there has been a continuous demand for their better characterization. Specifically, the characterization of hydrocarbons, fractions of petroleum crudes and gas condensate mixtures has been of more vital need in the industry. An ideal characterization factor when applied to pure hydrocarbons must be able to identify each component of every family (paraffinic, aromatic, naphthenic) of hydrocarbons uniquely by a distinct and specific number. Then, when applied to characterize fractions of a petroleum fluid it will have the capability of identifying each fraction distinctly.

Several characterization factors have already been defined by various investigators for determining the composition of complex hydrocarbon mixtures. While these factors have helped us to identify certain petroleum fluid fractions for some particular applications they still do not possess the ability to uniquely identify every distinct hydrocarbon. Some of these available characterization factors are described below.

Watson Characterization Factor (K_W)

The Watson characterization factor, K_W (Wauquier, 1995; Nelson, 1978), is probably the oldest of such factors and it is defined as:

$$K_W = \frac{(1.8T_b)^{1/3}}{S} \tag{1}$$

in which T_b is the boiling temperature (in kelvins) and S is the standard specific gravity (15.6°/15.6° C). This characterization factor, which was initially introduced by the research personnel of the *Universal Oil Products Company (UOP)*, is based on the observation that specific gravities of hydrocarbons are related to their H/C ratio (hydrogen-to-carbon ratio of the molecule) and as a result to their chemical character, and that their boiling points are linked to the carbon number of their molecules. Therefore, K_W of the pure components was defined using only their densities and boiling points in the form of Equation (1). In Table 1 the range of values of this factor for three families of hydrocarbons, namely paraffinic, naphthenic and aromatic, are reported.

TABLE 1

Watson characterization factor (K_W) for different hydrocarbon families

Homologue series	K_W
Paraffins	13.1-13.5
Naphthenes	10.5-13.2
Aromatics	9.5-12.5

As it can be observed in this table there is an overlap between the ranges of this factor for various hydrocarbon families. As a result, the use of this factor will not allow us to identify every hydrocarbon uniquely by a number.

Viscosity Gravity Constant (*VGC*)

The viscosity gravity constant *(VGC)* is defined in the following forms (Gruse and Stevens, 1960):

$$VGC = \frac{10S - 1.0752\log(V_1 - 38)}{10 - \log(V_1 - 38)} \tag{2}$$

or:

$$VGC = \frac{S - 0.24 - 0.22\log(V_2 - 38)}{0.755} \tag{3}$$

where V_1 and V_2 are Saybolt universal viscosities at 100° and 210°F, respectively. This characterization factor was originally developed to characterize oil types. *VGC* is of particular value in indicating a predominantly paraffinic of cyclic composition of the petroleum fluids. In fact this parameter is proposed to characterize oil types such as paraffinic, naphthenic, or aromatic hydrocarbons. This characterization factor cannot be defined for the light hydrocarbons since they are at a vapor state at 100° and 210°F.

Refractivity Intercept (*RI*)

The refractivity intercept *(RI)* is defined as (Sachanen, 1945):

$$RI = n - d_{20}/2 \tag{4}$$

in which n is the sodium D-line refractive index and d is the density of hydrocarbons in grams per cubic centimeter both at 20°C and 1-atm pressure. Kurtz and coworkers found out that if refractive indices of hydrocarbons are plotted against the respective densities, straight lines of constant slope are obtained, one for each homologue series (Gruse and Stevens, 1960), and this observation was the basic idea for the qualitative determination of the petroleum fluids composition, because the *RI* values for different hydrocarbon groups are different. For example its range of variations for the paraffins is 1.048 to 1.050, whereas for the aromatic hydrocarbons this range is 1.070 to 1.105.

Refractive Index Parameter *(I)*

This parameter is defined as follows:

$$I = \frac{n^2 - 1}{n^2 + 2} \tag{5}$$

As seen from the above equation, this parameter is only a function of the refractive index of the sample. This parameter, which was defined originally by Huang has a specific range for a certain hydrocarbon family. Therefore, similar to the above-mentioned parameters, this parameter can also represent the composition of petroleum fluids.

There are a number of other characterization factors which are used in the oil industry for various other purposes which are not related to the present discussion.

1 THE NEW CHARACTERIZATION FACTOR

One of the well-known equations in physics that is based on electromagnetic theory is the Lorentz-Lorenz Equation (Shoemaker *et al.*, 1996; Le and Weers, 1995). This equation gives the molar refraction, R, in the following form:

$$R = \frac{4\pi\alpha N_A}{3} = \frac{M}{d}\left(\frac{n^2 - 1}{n^2 + 2}\right) \tag{6}$$

where α is the distortion polarizability, N_A is Avogadro's number, M is the molecular weight, d is the density and n is the index of refraction. Molar refraction can be predicted by the group contribution methods, *i.e.* by addition of the molar refractions, R_i, of atoms and bonds existing in a molecule (CRC, 1980). Using the values given in the CRC handbook for different atoms and bonds and considering the general formula for different hydrocarbon series, the ratio *R/M* is calculated for homologues series of compounds which are presented as follows:

$$\left(\frac{R}{M}\right)_{\text{Par.}} = \frac{(R)_{C_N H_{2N+2}}}{(M)_{C_N H_{2N+2}}} = \frac{2.591N + (2N+2)1.028}{14.026N + 2.016} = \frac{4.47N + 2.056}{14.026N + 2.016} \tag{7}$$

$$\left(\frac{R}{M}\right)_{\text{Naph.}} = \frac{(R)_{C_N H_{2N}}}{(M)_{C_N H_{2N}}} = \frac{2.591N + (2N)1.028}{14.026N} = 0.33 \tag{8}$$

$$\left(\frac{R}{M}\right)_{\text{Aro.}} = \frac{(R)_{C_N H_{2N-6}}}{(M)_{C_N H_{2N-6}}} = \frac{2.591N + (2N-6)1.028}{12.01N + (2N-6)1.0079} = \frac{4.64N - 6.168}{14.027N - 6.047} \tag{9}$$

The values of *R/M* for three homologue series of hydrocarbons have been calculated using Equations (7)-(9) and the results are given in Table 2.

As can be seen from Table 2, values of the ratio *R/M* for different hydrocarbon series are completely distinct and no overlap is seen among them. Also it is seen from Table 1, that:

$$\left(\frac{R}{M}\right)_{\text{Aro.}} < \left(\frac{R}{M}\right)_{\text{Naph.}} < \left(\frac{R}{M}\right)_{\text{Par.}} \tag{10}$$

Although it is seen that *R/M* is a suitable parameter for separating different hydrocarbon series and that therefore it can be proposed as a new and satisfactory characterization factor, neither R nor M are measurable directly for a complex hydrocarbon mixture or petroleum fractions. To overcome this difficulty we rearrange Equation (1) and use Equation (5) to have:

$$\frac{R}{M} = \frac{I}{d} \tag{11}$$

According to Equation (6), the ratio *R/M*, which is not directly measurable for an unknown mixture, could be readily obtained from the measurement of the right-hand side of this equation. In other words, because *R/M* is equal to *I/d*, therefore from the measurement of the refractive index and density of the sample, one can find the ratio *I/d* instead of the measurement of the molar refraction, R, and molecular weight of the sample, which are more complex than the above-mentioned parameters, *i.e.* n and d.

2 RESULTS AND DISCUSSION

The ratio *I/d* is also an appropriate characterization factor for different homologue series of hydrocarbons. For justification of this point we have used the data of TRC (1986) and it is seen that the ratio *R/M* is very close to *I/d* for paraffinic hydrocarbons (normal alkanes). On the other hand this parameter has been calculated by the available correlations for naphthenic and aromatic hydrocarbons (Riazi and Al-Sahhaf, 1995). The results of the comparison between the calculated *R/M* and *I/d* parameters are shown in Table 2. One of the advantages of this parameter is its correspondence with the Lorentz-Lorenz Equation, which has a solid theoretical basis.

TABLE 2

Calculated *R/M* and correlated *I/d* for various homologue series of C_n (n = 1 to 40)

C_n	$(R/M)_{Par}$*	$(I/d_{20})_{Par}$**	$(R/M)_{Naph}$*	$(I/d_{20})_{Naph}$**	$(R/M)_{Aro}$*	$(I/d_{20})_{Aro}$***
1	0.418	0.410				
2	0.377	0.377				
3	0.363	0.363				
4	0.355	0.363				
5	0.351	0.350	0.331	0.329		
6	0.347	0.347	0.331	0.330	0.278	0.338
7	0.345	0.345	0.331	0.330	0.286	0.337
8	0.343	0.343	0.331	0.330	0.292	0.337
9	0.342	0.342	0.331	0.330	0.297	0.336
10	0.341	0.341	0.331	0.330	0.300	0.336
11	0.340	0.340	0.331	0.331	0.303	0.335
12	0.339	0.339	0.331	0.331	0.306	0.335
13	0.339	0.339	0.331	0.331	0.308	0.335
14	0.339	0.338	0.331	0.331	0.309	0.334
15	0.338	0.338	0.331	0.331	0.311	0.334
16	0.338	0.337	0.331	0.331	0.312	0.334
17	0.337	0.337	0.331	0.331	0.313	0.334
18	0.337	0.336	0.331	0.331	0.314	0.334
19	0.337	0.336	0.331	0.331	0.315	0.333
20	0.336	0.338	0.331	0.331	0.316	0.333
21	0.336	0.336	0.331	0.331	0.317	0.333
22	0.336	0.335	0.331	0.331	0.318	0.333
23	0.335	0.335	0.331	0.331	0.318	0.333
24	0.335	0.335	0.331	0.331	0.319	0.333
25	0.335	0.335	0.331	0.331	0.319	0.333
26	0.335	0.335	0.331	0.331	0.320	0.333
27	0.335	0.334	0.331	0.331	0.320	0.333
28	0.335	0.334	0.331	0.331	0.321	0.333
29	0.334	0.334	0.331	0.331	0.321	0.333
30	0.334	0.334	0.331	0.331	0.321	0.332
31	0.334	0.334	0.331	0.331	0.322	0.332
32	0.334	0.334	0.331	0.331	0.322	0.332
33	0.334	0.334	0.331	0.331	0.322	0.332
34	0.334	0.334	0.331	0.331	0.322	0.332
35	0.334	0.334	0.331	0.331	0.323	0.332
36	0.334	0.334	0.331	0.331	0.323	0.332
37	0.334	0.334	0.331	0.331	0.323	0.332
38	0.334	0.334	0.331	0.331	0.323	0.332
39	0.334	0.333	0.331	0.331	0.324	0.332
40	0.334	0.333	0.331	0.331	0.324	0.332

* Calculated from Equations (7)-(9).
** TRC (1986) data.
*** Calculated values from the correlations of Riazi and Al-Sahhaf (1995).

TABLE 3

Worked examples for ternary systems of carbon: tetrachloride (1), pyridine (2), ethylacetate (3) at different compositions, at 303.5 K

Mixture No.	Composition	Characterization factor	Mixture property (exp.)	Mixture property (cal.*)	Relative error (%)
Mixture 1	$x_1 = 0.4045$	Huang charac. factor *(I)*	$I_m = 0.2509$	$I_m = 0.2513$	0.16
	$x_2 = 0.1011$	Refractivity intercept *(RI)*	$RI_m = 0.8289$	$RI_m = 0.8572$	3.41
	$x_3 = 0.4944$	New charac. factor *(I/d)*	$(I/d)_m = 0.2137$	$(I/d)_m = 0.2140$	0.14
Mixture 2	$x_1 = 0.4026$	Huang charac. factor *(I)*	$I_m = 0.2653$	$I_m = 0.2658$	0.19
	$x_2 = 0.3030$	Refractivity intercept *(RI)*	$RI_m = 0.8426$	$RI_m = 0.8761$	3.98
	$x_3 = 0.2944$	New charac. factor *(I/d)*	$(I/d)_m = 0.2208$	$(I/d)_m = 0.2207$	0.04
Mixture 3	$x_1 = 0.4002$	Huang charac. factor *(I)*	$I_m = 0.2820$	$I_m = 0.2802$	0.63
	$x_2 = 0.5039$	Refractivity intercept *(RI)*	$RI_m = 0.8619$	$RI_m = 0.8949$	3.83
	$x_3 = 0.0959$	New charac. factor *(I/d)*	$(I/d)_m = 0.2290$	$(I/d)_m = 0.2280$	0.43

* For calculation of the Huang characterization factor and refractivity intercept parameter of the mixture, Kay's rule has been applied whereas for calculation of the new characterization factor for the mixture, $(I/d)_m$, the new proposed mixing rule *(Eq. (13))* has been applied.

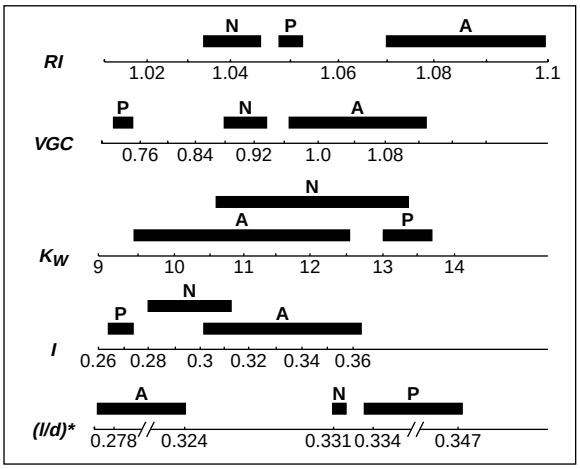

Figure 1

Comparison of different characterization factors.
(* Calculated values)

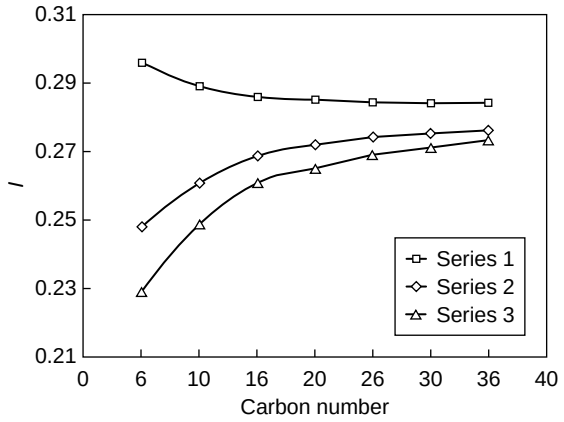

Figure 2

Huang characterization factor *(I)* for different homologue series.

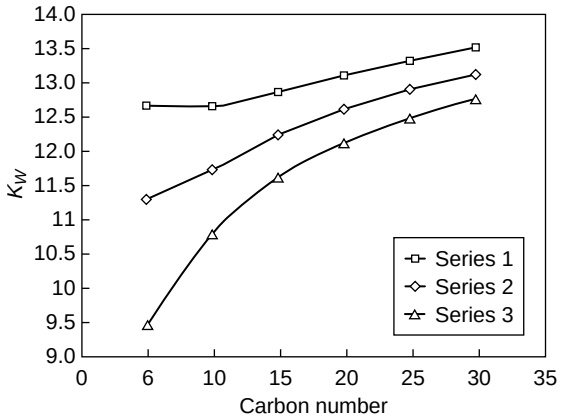

Figure 3

Watson characterization factor (K_w) for different homologue series.

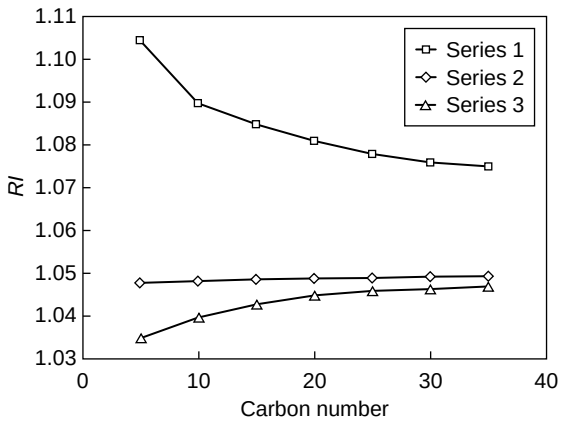

Figure 4

Refractivity intercept parameter *(RI)* for different homologue series.

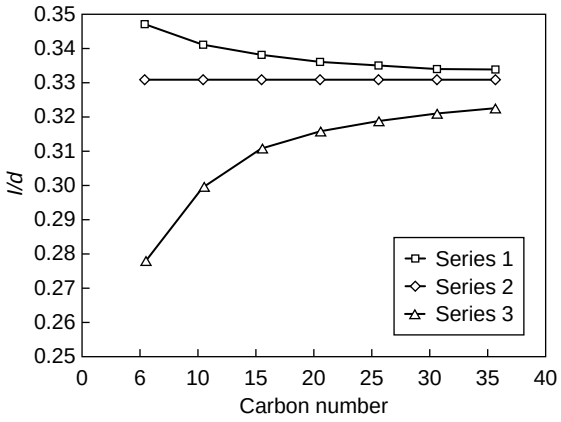

Figure 5

The proposed characterization factor (*R/M = I/d*) for different homologue series.

According to Bhatti *et al*. (1995), the Lorentz-Lorenz Equation for mixtures can be presented in the following form:

$$\frac{{n_{\text{mix}}}^2 - 1}{{n_{\text{mix}}}^2 + 2} V_{\text{mix}} = \sum \frac{n_i^2 - 1}{n_i^2 + 2} V_i \varphi_i \qquad (12)$$

If we assume $V_{\text{mix}} = M_{\text{mix}}/d_{\text{mix}}$ and $V_i = M_i/d_i$, the following equation is then proposed:

$$\left(\frac{I}{d}\right)_{\text{mix}} = \frac{1}{M_{\text{mix}}} \sum \left(\frac{I}{d}\right)_i M_i \varphi_i \qquad (13)$$

We have compared this new mixing rule with the Kay's rule applied for different characterization factors and the results are given in Table 3. As can be seen from this table, Equation (13) is better than Kay's rule for calculation of the mixture mean property, $(I/d)_{\text{mix}}$, using the property of the species existing in the mixture.

On the other hand we have compared this new characterization factor with the others, such as the viscosity gravity constant *(VGC)*, Watson characterization factor (K_w), refractive index parameter *(I)*, and the refractivity intercept parameter *(RI)* in Figure 1. The variations of different characterization factors *versus* carbon number are shown in Figures 2 to 5. As can be seen from Figure 1, K_w and *I* cannot separate completely the various hydrocarbon series from each other. Therefore these factors are not good enough for the characterization of hydrocarbons. On the other hand, as shown in Figure 1, *RI* and *VGC* can separate the homologue series of hydrocarbons but these two parameters could not continuously represent the various homologue series and some parts of the range of *RI* and *VGC* have no significance for any specific type of hydrocarbons, while the new characterization factor *(I/d)* separates the various hydrocarbon series and the blank space between different hydrocarbon groups is relatively small. Therefore it seems that this parameter is to be preferred over the other characterization factors available.

Considering the above results and discussion, it is concluded that the characterization factor *(I/d)* proposed here is a suitable tool for the characterization of hydrocarbons. It is easily measurable and it has a sound theoretical basis, which can be used to characterize petroleum fluid fractions.

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