Structural modeling of petroleum fractions based on mixture viscosity and Watson K factor

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Abstract−Two procedures have been developed for structural modeling of petroleum fractions based on mixture viscosity and Watson K factor. The representative molecules of paraffinic, naphthenic and aromatic hydrocarbons, based upon Ruzicka's structural model, have been determined for lube-oil cut SAE 10 from Tehran oil refinery. Unlike previous methods, the newly developed procedures do not require time-consuming and costly laboratory data such as true boiling point profile. Good agreement between predictions of the new models and experimental results has been observed. Moreover, the proposed methods take less run-time than previous models due to less experimental and computational complexities. The results indicate that Ruzicka's procedure, based on vapor pressure, is only applicable for light hydrocarbon mixtures, while the new methods can be applied for structural modeling of a wide range of petroleum fractions. Furthermore, as a result of this study, the application of a vapor pressure constraint leads to a higher degree of accuracy than the earlier suggested constraint, partial pressure, by Ruzicka.

Key words: Characterization, Petroleum, Representative Molecule, Structural Modeling, Viscosity

INTRODUCTION

Characterization of petroleum fractions is an essential step in many processes in which one is trying to determine the optimum operating conditions. Unlike light fractions, it is rather impossible to determine the distribution and chemical structure of different species in heavy fractions, due to the large number of components and complexity of the mixtures. Nonetheless, in recent years more experimental and computational techniques have been suggested in the literature for characterization of heavy fractions [1-6].

In general, there are three main approaches for modeling of hydrocarbon fractions using bulk properties:pseudo-component, continuous and structural modeling (SM). According to the first method, constituents of each hydrocarbon family are grouped together as a single pseudo-component [7-10]. Generally, hydrocarbon fractions are modeled into three pseudo-components from three homologous groups of n-Alkanes, n-Alkylcyclopentanes (or n-Alkylcyclohexanes) and n-Alkylbenzenes, having the same boiling point temperature (T_B) as that of ASTM D86 at 50% [11]. The continuous method presents the composition of hydrocarbon fractions as a distribution function of independent variables [12,13]. These independent variables are selected among measurable properties such as T_B, molecular weight (MW) and density (d). Despite the simplicity, these methods are unable to present chemical structure of species and are not applicable when the usage of molecular structures is inevitable. SM approaches try to model the fractions through dividing the mixture into several homologous groups and defining some representative molecules for each homologous series. For example, Hu et al. [14] defined a molecular matrix based on a homologous series of hydrocarbons, which contains all possible available components. Unfor-

tunately, for medium and heavy fractions such matrices are large enough to lead to serious problems at structural modeling stage. In this method, the set of representative molecules is selected from real organic components (e.g., hexane and toluene) which may vary in different petroleum fractions. Thus, the molecular matrices are unique for each fraction and screening of species requires sufficient experience.

Another set of representative molecules has been presented by Ruzicka et al. [15] which are unique for all fractions and in artificial forms (Fig. 1). In contrast to Hu's procedure, the numbers of functional groups in Ruzicka's artificial molecules are unknown and can assume real or non-integer values. Ruzicka et al. divided the present species to paraffins (P), naphthenes (N), aromatics (A) groups and then proposed representative molecule for each group. They used this model to study liquid-liquid equilibrium (LLE) for gaso-
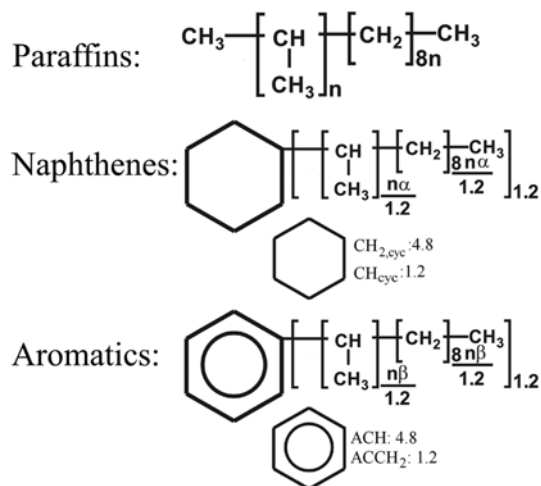

Fig. 1. Ruzicka's structural models.

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line-methanol system. They determined structural parameters (n, α, and β) using an objective function (OF) based on gasoline vapor pressure. Also, Vakili-Nezhaad et al. applied this structural model to study the extractive dearomatization of lube-oil cut [16]. However, Vakili-Nezhaad et al. developed their own OF on the base of MW. Espada et al. modified Ruzicka's models for LLE study of vacuum distillate-furfural mixture [17]. Following Vakili-Nezhaad's procedure, they used MW adjusting to determine n, α, and β.

However, the above-mentioned procedures require true boiling point (TBP) data, while such input data are practically scarce in literature and their measurement is more difficult than other properties, such as viscosity and density. Therefore, the main emphasis in this work is on the structural modeling of petroleum fractions utilizing minimum and easily measurable laboratory data.

MODELING PROCEDURE

Using Smith's findings [18] on carbon-type distribution in hydrocarbon cuts, Ruzicka et al. [19] proposed a representative structure for P, N, and A hydrocarbons (see Fig. 1). For modeling of gasoline, however, they did not consider the fused ring aromatic carbons due to low T_B of gasoline [15]. Nevertheless, it has been observed that proposed models also showed an acceptable degree of accuracy for heavier fractions [16]. As shown in Fig. 1, these models contain three structural parameters (n, α, and β) which can be determined using various approaches.

1. Vapor Pressure Approach

Ruzicka et al. [15] used the following OF to adjust the structural parameters, where P, x_i and T denote the vapor pressure of the real mixture, mole fraction of i-th compound of the model and temperature, respectively. Also, P_i^0 is the vapor pressure of i-th compound of the model, which can be estimated through AMP (Abrams-Massaldi-Prausnitz) group contribution method [20]. Meanwhile, they applied two constraints to ensure that the vapor pressures of the compounds do not differ substantially.

$$OF_{P1} = P - \sum_{i=P,N,A} x_i P_i^0(n, \alpha, \beta, T) \tag{1}$$

$$x_1 P_1^0(n, \alpha, \beta, T) - x_2 P_2^0(n, \alpha, \beta, T) = 0 \tag{2}$$

$$x_1 P_1^0(n, \alpha, \beta, T) - x_3 P_3^0(n, \alpha, \beta, T) = 0 \tag{3}$$

In the present study, Ruzicka's molecular models were used to model the lube-oil cut from a Tehran oil refinery. However, its heavier constituents are believed to be non-ideal mixtures. Thus, the OF was modified as Eq. (4) and the UNIFAC model was applied to adjust non-ideality. Ruzicka et al. used mean average boiling point (MeABP) in lieu of T_B curve. This means that all existing components in the mixture must have similar vapor pressure and the mixture must behave as a pure liquid hydrocarbon (Eqs. (2) and (3)). However, it is clear that the satisfaction of these equations leads to equality of the partial pressures. Therefore, here, the constraints were changed as follows and the maximum acceptable variance between the vapor pressures was selected as 10^{-4}.

$$OF_{P2} = P - \sum_{i=P,N,A} x_i \gamma_i P_i^0(n, \alpha, \beta, T) \tag{4}$$

$$P_1^0(n, \alpha, \beta, T) - P_2^0(n, \alpha, \beta, T) = 0 \tag{5}$$

$$P_1^0(n, \alpha, \beta, T) - P_3^0(n, \alpha, \beta, T) = 0 \tag{6}$$

2. Molecular Weight Approach

Vakili-Nezhaad et al. [16] used an OF based on average MWs. They applied versatile Riazi's distribution model [12] and Riazi-Daubert's MW correlation [11], Eq. (7), to convert TBP data to MW distribution function as Eq. (8), where T_B, SG and N_C are the absolute boiling point (K), specific gravity and carbon number.

$$MW = 1.66069 \times 10^{-4} \times T_B^{2.1962} SG^{-1.0164} \tag{7}$$

$$W_i = A_i (14.0268 N_C - B_i)^{C_i} \exp\left[-\left(\frac{14.0268 N_C - B_i}{D_i}\right)^{1+C_i}\right]$$
$$i = P, N, A \tag{8}$$

By applying probability density function, the average MWs of P, N, and A hydrocarbons were calculated 328.18, 291.89 and 271.16, respectively, and the OF was defined as:

$$OF_{MW} = [328.18 - MW_P^{model}]^2 + [291.89 - MW_N^{model}]^2$$
$$+ [271.16 - MW_A^{model}]^2 \tag{9}$$

3. Vapor Pressure and Molecular Weight Approach

It is expected that the adjustment of more variables leads to improvement in accuracy of the structural models. Thus, here, a new OF consisting of both vapor pressure and molecular weightwas studied to improve the accuracy of the structural models. Meanwhile, similar to section 1, the effects of thermodynamic non-ideality (γ variable in Eq. (4)) and different optimization constraints (vapor pressure and partial pressure constraints) were also investigated.

4. Viscosity Approach

As shown above, for structural modeling through both Ruzicka and Vakili-Nezhaad procedures, the TBP (or MeABP) data applying is inevitable. The measurement of these properties is tedious and the proposed correlations generally do not provide an acceptable degree of accuracy [11]. Therefore, a new OF was suggested based on mixture viscosity due to its simple and rapid measurability. The viscosity is one of the most commonly used characterization factors for medium and heavy fractions [11] thus, the newly proposed OF can be applied for a wide range of mixtures.

$$OF_\nu = \sum_{i=1,2,\ldots} [\nu_{T_i}^{exp.} - \nu_{T_i}^M(n, \alpha, \beta, T)]^2 \tag{10}$$

where $\nu_T^{exp.}$ and ν_T^M are kinematic viscosities of the real and model mixtures at temperature T. Since adjusting of ν brings about the adjustment of both dynamic viscosity and density, the OF was pre-

Table 1. Coefficients B_{m0} and B_{m1} and correlation coefficient (r) as a function of hydrocarbon class [21]

Compound class[a]	B_{m0}	B_{m1}	r
n-Paraffins, 1-olefines	−12.067	3.110	0.98
Branched paraffins and olefins	−10.976	2.668	0.96
Nonfused aromatics	−9.692	2.261	0.87
Fused-ring aromatics	−9.309	2.185	0.82
Nonfused naphthenes	−9.001	2.350	0.90
Fused-ring naphthenes	−9.513	2.248	0.87

[a]Based on 1300 individual μ in the range 283 to 473 K, of 273 heavy hydrocarbons (MW>100)

sented in kinematic viscosity form. The dynamic viscosities of P, N and A hydrocarbons (in mPa·s) at temperature T (in K) were estimated by Mehrotra's correlation (Eq. (11)) where B_{m0} and B_{m1} are compound-class coefficients [21], as shown in Table 1.

$$\log_{10}[\mu+0.8]=100[0.01T]^{B_m} \tag{11}$$
$$B_m=B_{m_0}+B_{m_1}\log_{10}MW(n,\alpha,\beta)$$

Mehrotra then proposed Eq. (12) for calculating B_m based on effective carbon number (ECN) [22].

$$B_m=-5.745+0.616\times Ln(ECN)-40.468\times(ECN)^{-1.5} \tag{12}$$

Their reported ECN versus carbon number (N_C) for P, N and A families can well be fitted in straight lines represented as follows.

$$ECN_P=0.989\times N_{C,P}-0.270\ (R^2=0.996)$$
$$ECN_N=N_{C,N}+1.795\ (R^2=0.967)$$
$$ECN_A=0.928\times N_{C,A}+1.652\ (R^2=0.978)$$

Finally, following mixing rule [23] was used to calculate viscosity of model mixture.

$$\mu_{mix.}=\left(\sum_{i=P,N,A}\left(x_i\mu_i^{\frac{1}{3}}\right)\right)^3 \tag{13}$$

where x_i denotes mole fraction of i-th component. It is necessary to convert the estimated values of dynamic viscosity to the kinematic form. Table 2 shows the bulk properties of studied fraction [16]. Unfortunately, temperature dependency of mixture density (d_{mix}) has not been reported by Vakili-Nazhaad et al. [16]. Therefore, the following procedure was proposed to resolve this problem.

In general, both d_{mix} and refractive index (n_D) are temperature dependent, but the molar refraction (R_m) is almost temperature independent [24]. Therefore, having d_{mix} at 15.5 °C, the following equations [11] were used to estimate d_{mix} at other temperatures.

$$R_m=\left(\frac{MW}{d}\right)\left(\frac{n_D^2-1}{n_D^2+2}\right) \tag{14}$$

$$n_D^T=n_D^{20}-0.0004\times(T-293.15) \tag{15}$$

5. Watson K Factor Approach

In addition to OF_v (Eq. (10)), the problem was also reformulated

based on Watson K factor (K_W). This factor is used extensively in characterization of petroleum fractions with rather small variation within each hydrocarbon family [25-28]. Therefore, the following average values of K_W were estimated for P, N, and A hydrocarbons: 12.7619, 11.0000, and 10.3650. Then, the new OF was defined as:

$$OF_{K_W}=[12.7619-K_{W,P}^M(n,\alpha,\beta)]^2+[11.0000-K_{W,N}^M(n,\alpha,\beta)]^2$$
$$+[10.3650-K_{W,A}^M(n,\alpha,\beta)]^2 \tag{16}$$

where $K_{W,i}^M$ denotes K_W of i-th compound of the model and was related to n, α, and β through boiling point ($K_W=(1.8T_B)^{1/3}/SG_{15.5\,°C}$). The boiling point can be evaluated from MW (merely a function of n, α, and β) and Huang's characterization factor ($I=(n_D^2-1)/(n_D^2+2)$) or SG through the following equations [11].

$$T_{B,i}=9.3369\times \exp[1.6514E-4MW_i(n,\alpha,\beta)+1.4103SG_i-7.5152E$$
$$-4MW_i(n,\alpha,\beta)\times SG_i]\times MW_i(n,\alpha,\beta))^{0.5369}SG_i^{-0.7276} \tag{17}$$

$$T_{B,i}=75.775\times(MW_i(n,\alpha,\beta)^{0.4748}I_i^{0.4283} \tag{18}$$

Accordingly, it is necessary to determine SG_i, I_i, and MW_i of P, N, and A hydrocarbons existing in the fraction. Required properties were estimated through the newly proposed algorithm (Fig. 2).

6. Carbon and Hydrogen Content Approach

Two of the most important data for hydrocarbon mixtures, carbon to hydrogen weight ratio (COH) and total hydrogen content (THC), depend on the type of existent hydrocarbons and MW (in other words n, α, and β) that can easily be measured. Also, in absence of experimental data, some correlations have been presented in order to estimate COH and THC [2,3,11,29-31]. Thus, the following OF was proposed:

$$OF_{COH+THC}=[COH_{mix.}^{exp.}-COH_{mix.}^{Model}(n,\alpha,\beta)]^2$$
$$+[THC_{mix.}^{exp.}-THC_{mix.}^{Model}(n,\alpha,\beta)]^2 \tag{19}$$

It worth mentioning that since C and H are the predominant elements in these mixtures, we assumed that molecules generally consist of these elements. COH and THC of the molecular models were determined as a function of n, α, and β through structural models (see Fig. 1).

Table 2. Physical properties of studied fraction [16]

Property	Measured value
Kinematic viscosity at 40 °C (cSt)	32.19
Kinematic viscosity at 100 °C (cSt)	4.93
Specific gravity (15.5 °C/15.5 °C)[a]	0.9134
Refractive index (at 20 °C and 1 atm)	1.5058
PNA composition, wt% (mol%)	
Paraffins (P)	0.491 (0.455)
Naphthenes (N)	0.332 (0.346)
Aromatics (A)	0.177 (0.199)
True boiling point (TBP), ASTM D2887[b]	

wt%	IBP	10	20	30	40	50	60	70	80	90	EBP
T (°C)	281.3	350.6	370.2	381.7	390.7	398.3	405.3	412.5	420.2	429.4	464.7

[a]Specific gravity (SG) can be converted to density (at 20 °C) as follow: d=(SG−0.01044)/0.9915 [11]. (d_{mix}=0.9107 g cm⁻³)
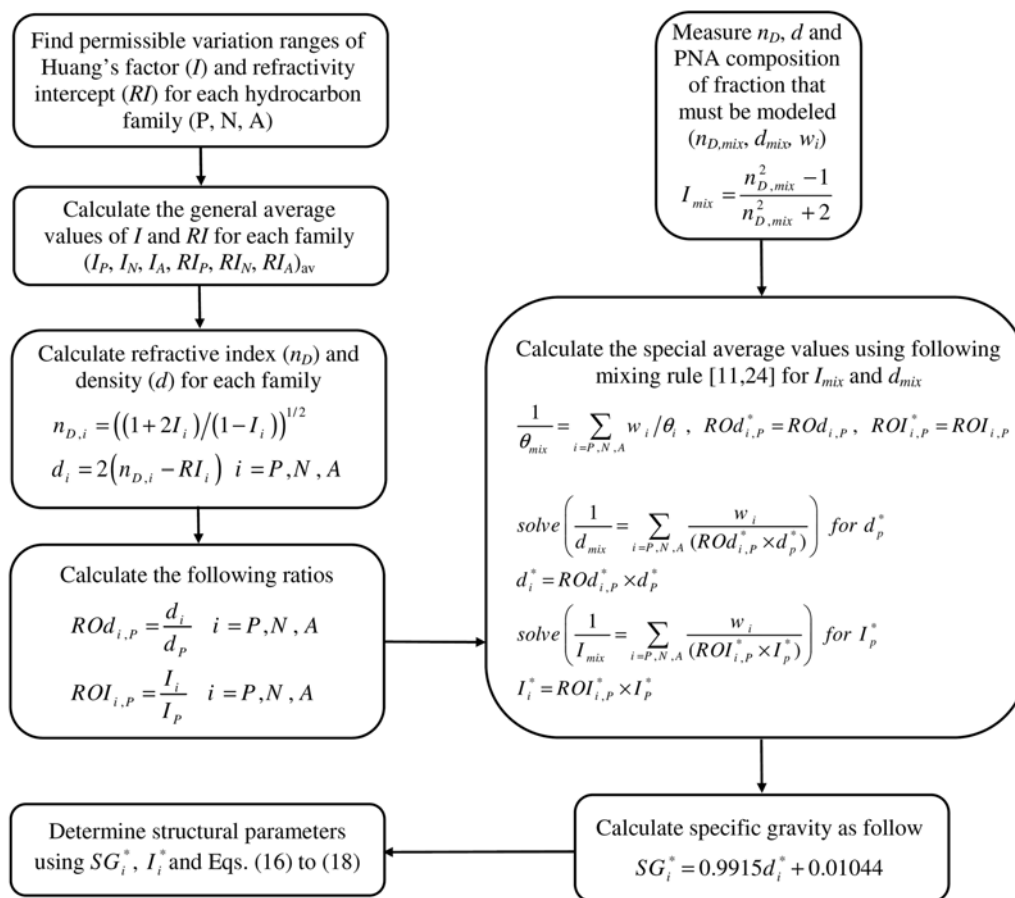[b]Detailed TBP data have been reported by Vakili-Nazhaad et al. [16]

Fig. 2. K_W adjusting algorithm for structural modeling of petroleum fractions (present study).

VALIDATION OF STRUCTURAL MODELS

Due to the complexity of the petroleum fractions, there are very few methods that can be applied to validate molecular models. LLE modeling is the most frequently used for this purpose [15-17]. Since the exact prediction of all components existing in these mixtures is nearly impossible, composition data are generally reported as PNA, which brings about very poor data and provides minimum knowledge of the composition. Vakili-Nezhaad et al. usedthe PNA approach to estimate the composition of the immiscible phases in dearomatization of lube-oil cut by NMP [16]. The reported data are doubtful and exhibit significant deviations from mass conservation. In other words, the feed, raffinate and extractpoints cannot lie on a straight line in three dimensions. Thus, here, new alternative properties were used for validation of molecular model. It is clear that these properties must obligatory be defined as a function of structural parameters. Among physical properties, n_D is a very useful characterization factor, especially in relation with molecular structure and composition. Eqs. (20) and (21) [11,24] were used to estimate n_D of representative molecules.

$$\frac{(n_D^2-1)}{(n_D^2+2)} = 0.26376 \times \exp[1.7458\mathrm{E}-2\,\nu_{38}(n,\alpha,\beta) + 0.231043\mathrm{SG}$$
$$-1.8441\mathrm{E}-2\,\nu_{38}(n,\alpha,\beta) \times \mathrm{SG}]$$
$$\times(\nu_{38}(n,\alpha,\beta))^{-0.01128}\mathrm{SG}^{0.77078} \tag{20}$$

$$\mathrm{SG}=1.1284\mathrm{E}6\times\exp[-1.588\mathrm{E}-3\mathrm{MW}(n,\alpha,\beta)$$

$$-20.594\frac{(n_D^2-1)}{(n_D^2+2)} + 7.344\mathrm{E}-3\times\mathrm{MW}(n,\alpha,\beta)\frac{(n_D^2-1)}{(n_D^2+2)}\Bigr]$$
$$\times(\mathrm{MW}(n,\alpha,\beta))^{-7.71\mathrm{E}-2}\Bigl(\frac{(n_D^2-1)}{(n_D^2+2)}\Bigr)^{6.3028} \tag{21}$$

Also, Eqs. (11) to (13) were applied to calculate kinematic viscosity, another useful property for medium and heavy fractions. Note that the viscosity was used to compare all objective functions apart from the one for viscosity approach. Eventually, a more general comparison was done by using the estimated values of MW, T_B and other physical properties.

RESULTS AND DISCUSSION

MATLAB® software and the direct search procedure were used to find the optimum values of n, α, and β in a 3D solution space. A detailed result of the newly proposed algorithm (see Fig. 2) is summarized in Table 3. The mean absolute percentage errors between the general and special average values of I and SG are 4.12 and 5.28%, respectively. The results revealed that such deviations lead to a significant error in the optimum values of n, α, and β. As a major advantage of this algorithm, a more accurate estimation of physical propertiesis achieved through newly proposed modification of the required data.

It was observed that it is not possible to model the petroleum fractions through COH and THC (Eq. (19)). Regardless of type and

Table 3. Detailed results of the newly suggested algorithm (see Fig. 2)

Type	Rep. ranges for I_i^a	Cal. general $I_{av,i}$	$ROI_{i,P}$ $ROI^*_{i,P}$	Cal. special $I^{*b}_{av,i}$	Rep. ranges for RI_i^a	Cal. general $RI_{av,i}^c$	Rep. general $RI_{av,i}^d$	Cal. general $RI_{av,i}^e$	Cal. general $d_{av,i}^f$	$ROd_{i,P}$ $ROd^*_{i,P}$	Cal. special $d^{*bf}_{av,i}$	Cal. special $SG^{*b}_{av,i}$
P	0.260-0.273	0.2665	1	0.27795	1.048-1.050	1.0490	1.0482	1.0486	0.79416	1	0.83893	0.84224
N	0.278-0.308	0.2930	1.09944	0.30559	1.030-1.046	1.0380	1.0380	1.0380	0.91952	1.15785	0.97135	0.97353
A	0.298-0.362	0.3300	1.23827	0.34418	1.070-1.105	1.0875	1.0810	1.0843	0.97958	1.23348	1.03480	1.03644

[a]Huang's factor at 20 °C, reported by Riazi [11] (MW>200)
[b]Special average values for lube-oil cut SAE 10 from Tehran oil refinery (present study)
[c]Calculated general values from reported ranges of RI_i
[d]Reported by Riazi et al. [32] (200<MW<600)
[e]Average value of two previous columns
[f]Density at 20 °C (g cm^{-3})

Table 4. Optimum values of n, α, and β and chemical formula of representative molecules

Objective function	NRCT^c	Structural parameters			Representative molecules		
		n	α	β	Paraffins	Naphthenes	Aromatics
Molecular weight (MW)	48.8	2.1298	0.6407	0.5834	$C_{23.30}H_{48.60}$	$C_{20.85}H_{41.69}$	$C_{19.63}H_{35.65}$
Pressure-VP- ideal^a	52.3	2.1485	0.7317	0.6468	$C_{23.49}H_{48.97}$	$C_{22.92}H_{45.84}$	$C_{21.10}H_{38.59}$
Pressure-PP- ideal^b	53.6	2.2791	0.6989	0.5160	$C_{24.79}H_{51.58}$	$C_{23.13}H_{46.26}$	$C_{18.96}H_{34.32}$
Pressure-VP- non ideal	86.1	2.1558	0.7302	0.6440	$C_{23.56}H_{49.12}$	$C_{22.94}H_{45.88}$	$C_{21.08}H_{38.57}$
Pressure-PP- non ideal	87.5	2.2832	0.6939	0.5193	$C_{24.83}H_{51.66}$	$C_{23.04}H_{46.09}$	$C_{19.06}H_{34.51}$
Pressure+ MW-VP- ideal	72.2	2.0311	0.7117	0.6262	$C_{22.31}H_{46.62}$	$C_{21.66}H_{43.31}$	$C_{19.92}H_{36.24}$
Pressure+ MW-PP- ideal	73.6	2.1790	0.6754	0.4962	$C_{23.79}H_{49.58}$	$C_{21.92}H_{43.83}$	$C_{18.01}H_{32.42}$
Pressure+ MW-VP- non ideal	98.8	2.0311	0.7117	0.6262	$C_{22.31}H_{46.62}$	$C_{21.66}H_{43.31}$	$C_{19.92}H_{36.24}$
Pressure+ MW-PP- non ideal	100	2.1787	0.6753	0.4961	$C_{23.79}H_{49.57}$	$C_{21.91}H_{43.83}$	$C_{18.01}H_{32.42}$
Kinematic Viscosity	42.7	2.4649	0.5326	0.7128	$C_{26.65}H_{55.30}$	$C_{20.33}H_{40.66}$	$C_{24.77}H_{45.94}$
Watson K factor	48.3	2.1596	0.6503	0.5798	$C_{23.60}H_{49.19}$	$C_{21.24}H_{42.49}$	$C_{19.72}H_{35.84}$

[a]VP: vapor pressure constraint
[b]PP: partial pressure constraint
[c]Normalized required computation time

source, with few exceptions, it appears [11,33] that the compositions of the major elements existing in petroleum fractions vary over fairly narrow limits (e.g., C: 83-87, H: 10-14, N: 0.1-2, O: 0.05-1.5, and S: 0.05-6 wt%). Owing to this, Eq. (19) did not lead to a unique n, α, and β set for a special fraction. Unlike $OF_{COH+THC}$, other suggested OFs (Eqs. (10) and (16)) showed a generally acceptable degree of accuracy than the earlier published cases (Eqs. (1) and (9)). The optimum values of n, α, and β and the chemical formula of representative molecules are summarized in Table 4.

The variances (σ^2) between the obtained compositions of the C and H elements in the representative molecules show this trend: aromatics (σ_C^2=3.52, σ_H^2=14.10)>paraffins (σ_C^2=1.50, σ_H^2=6.01)> naphthenes (σ_C^2=0.90, σ_H^2=3.61). Thus, the structure of aromatic molecules demonstrated the highest sensitivity to the applied OF. Considering the roles that aromatics play in industrial issues, it is necessary to determine the most precise OF in the structural modeling of petroleum fractions.

Fig. 3 shows the effect of vapor and partial pressure constraints on the predicted ν and n_D. This figure reveals that the application of vapor pressure constraint leads to a higher degree of accuracy than the earlier suggested constraint, partial pressure, by Ruzicka. And although n_D is a very sensitive factor especially in relation with

structural groups and composition [11,24], it varies in a fairly narrow range. Therefore, a little change in n_D can represent a prominent alteration in the structural models (see Fig. 3 and also compare the chemical structure of representative molecules inthe second and third rows in Table 4).

Ruzicka's structural models (Fig. 1) have been developed based on the experimental data [18] available over a wide range of hydrocarbon mixtures. Thus, they can be applied in modeling of both light and heavy fractions. Nevertheless, unlike Ruzicka's structural models, his procedure (Eqs. (1) to (3)) inherently propels the behavior of hydrocarbon fractions into ideal behavior. As a reasonable assumption, the light fractions can be assumed as an ideal mixture, while the heavier constituents in medium and heavy cuts are believed to be non-ideal mixtures. Since applying the vapor pressure constraints (Eqs. (2) and (3)) in Ruzicka's procedure is compulsory, the non-ideality correction (γ parameter in Eq. (4)) in his procedure could not improve the precision of the property estimation and molecular structure (see Fig. 4 and Table 4). Consequently, this procedure cannot reach an acceptable degree of accuracy for medium and heavy fractions.

Fig. 5 shows the performance of the different objective functions in modeling of the studied mixture. As mentioned above, Ruz-
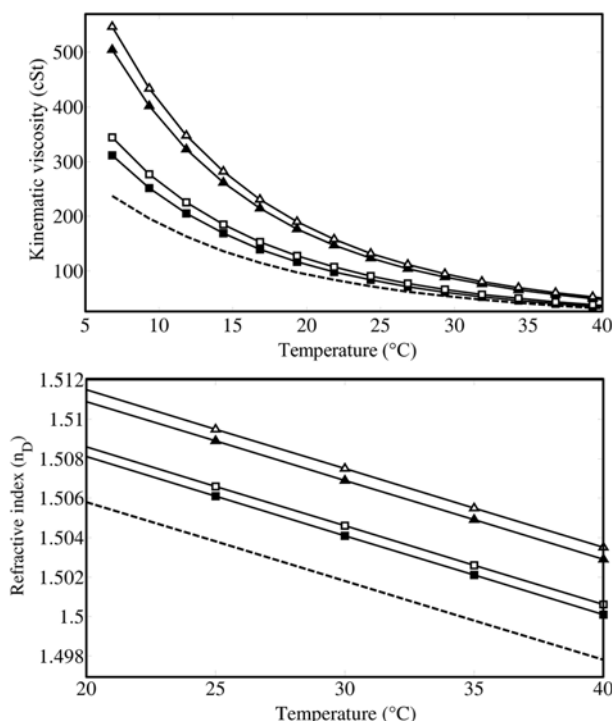
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Fig. 3. The effect of different constraints on estimated values of ν (cSt) and n_D for lube-oil cut from Tehran oil refinery (dash line: experimental data, ▲: vapor pressure approach with vapor pressure constraint, △: vapor pressure approach with partial pressure constraint, ■: vapor pressure and molecular weight approach with vapor pressure constraint, □: vapor pressure and molecular weight approach with partial pressure constraint).

Fig. 4. The effect of non-ideality correction on estimated values of ν (cSt) and n_D for lube-oil cut from Tehran oil refinery (dash line: experimental data, □: vapor pressure approach with ideal mixture assumption, ■: vapor pressure approach with non-ideal mixture assumption, △: vapor pressure and molecular weight approach with ideal mixture assumption, ▲: vapor pressure and molecular weight approach with non-ideal mixture assumption).

icka's procedure (entitled as vapor pressure approach) shows the maximum deviation from the experimental data. Also, two new proposed approaches as well as Vakili-Nezhaad's procedure can be applied for structural modeling on a wide range of petroleum fractions with an acceptable degree of accuracy. However, unlike Vakili-Nezhaad's procedure, newly developed procedures do not require time-consuming and costly laboratory data such as TBP profile. Note that the total run-time of the structural modeling problems can be divided into two parts: (1) required laboratory time to measure input experimental data and (2) required computation time. The major advantage of viscosity and K_W approaches isthat only a very small fraction of information is needed to define the problem. Indeed, the viscosity approach requires only two kinematic viscosities at different temperatures and PNA analysis of the fraction. Also, the K_W approach requires the mixture density and refractive index as well as PNA analysis,which practically are simpler in measurement than TBP distillation data. Therefore, the new procedures take less laboratory time to measure required experimental data than theprevious methods.

Moreover, as mentioned in section 2, the Vakili-Nezhaad procedure requires extensive analysis of the mixture and a large computation time for estimation of structural parameters. Also, heavier constituents of medium and heavy fractions are believed to be non-ideal mixtures. Thus, Ruzicka's procedure needs non-ideality correction through UNIFAC model, while such correction increases computational complexity and requires a large computation time to
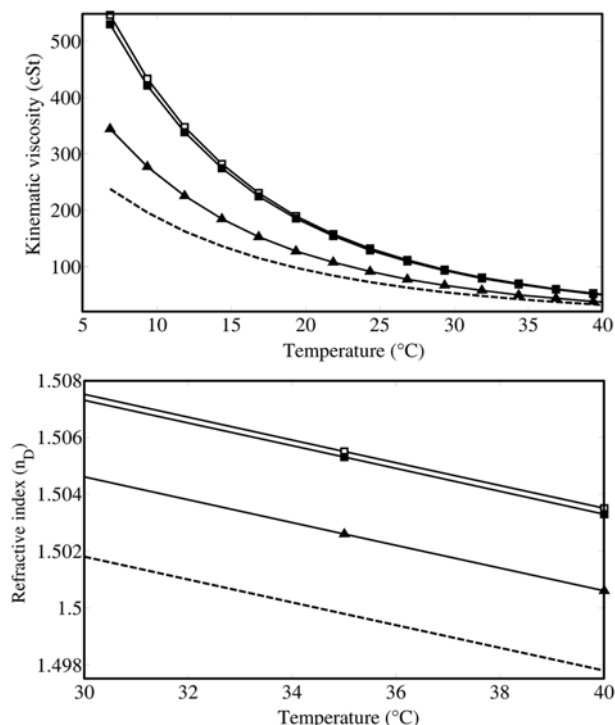
resolve this problem. Unlike previous methods, the new approaches have the advantage of shortening the computation run-time because of simplicity and lower data handling. Thus, it the viscosity and K_W approaches take less total run-time than previous models due to less experimental and computational complexity.

Table 5 shows the estimated values of some physical properties. The vapor pressure and MeABP at atmospheric pressure were calculated through AMP method [20]. The viscosities were estimated through Eqs. (11) to (13) and n_D at different temperatures was calculated by Eqs. (14), (15), (20), and (21). Also, Fig. 5 shows the temperature dependency of ν and n_D. It is expected that the adjustment of more variables leads to improvement in accuracy of the models. According to Fig. 5, despite elevated computational complexity, the new OF consisting of both vapor pressure and MW did not lead to higher degree of accuracy than MW adjusting function.

Similar to other characterization problems, the modification of previous methods can be divided into two parts: (1) improvement in accuracy of the modeling procedure, and (2) simplification of problem definition (or formulation). As shown in Tables 4 and 5, it is clear that the viscosity approach improves the accuracy of predicted properties, while the K_W approach has the same accuracy as previous procedures. However, unlike prior methods, both viscosity and K_W approaches do not require TBP data, while such input data are practically scarce in literature and their measurement is more difficult than other properties, such as viscosity, density and refrac-
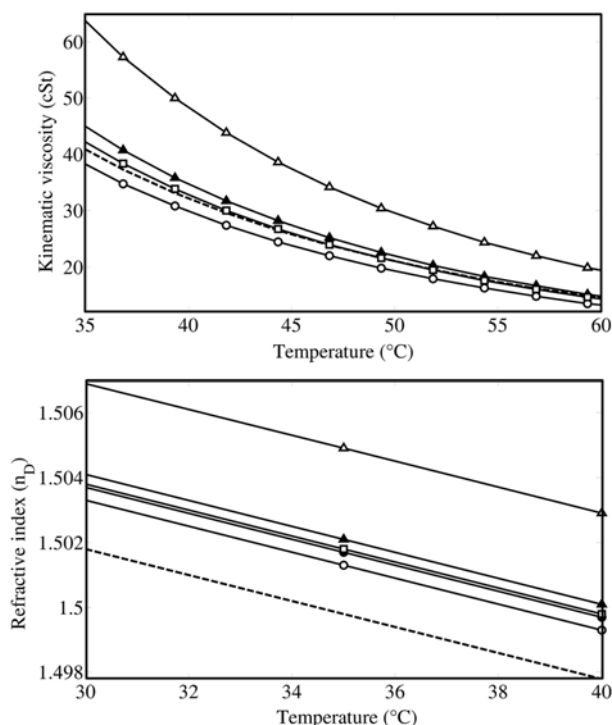
Fig. 5. The effect of different OFs on estimated values of ν (cSt) and n_D for lube-oil cut from Tehran oil refinery (dash line: experimental data, ○: molecular weight approach, △: vapor pressure approach with partial pressure constraint, ▲: vapor pressure and molecular weight approach, □: Watson K factor approach, ●: viscosity approach).

tive index. It means simplification of the problem definition (or formulation) with the same accuracy as prior procedures. Indeed, the viscosity approach not only improves accuracy of earlier published methods but also simplifies the formulation of SM problems. Also, the K_W approach can simplify problem formulation with the same

accuracy as previous procedures.

Ruzicka et al. used mean average boiling point in lieu of true boiling point curve [16], which means that all existing components in the mixture have the similar vapor pressure and the mixture has been assumed as an ideal mixture. Also, Vakili-Nezhaad et al. used Eq. (7) to develop MW distribution functions. This correlation fails to properly predict properties for hydrocarbons above C_{25} and it cannot simply extrapolate to heavier fractions [11]. Unlike Ruzicka's procedure, newly developed methods do not make any ideality assumptions. Moreover, unlike Vakili-Nezhaad's procedure, the viscosity estimation through Mehrotra's correlation can be reliably extrapolated to heavier fractions [22]. Thus, the new procedures can be used to structurally model a wide range of hydrocarbon fractions.

Structural modeling is generally applied to study LLE behaviors, such as thermodynamic modeling of extraction processes. In these operations, one customarily deals with mass transfer phenomena within/between two immiscible liquid phases. In these systems, spontaneous and forced alterations through diffusive and forced convective movements occur, ultimately bringing the entire system to a state of equilibrium, whereupon alteration stops. Diffusive movement is usually perused through diffusivity or diffusion coefficient (D_{ij}). For dilute solutions of nonelectrolytes, the following empirical correlation has been recommended by Wilke and Chang to estimate the diffusivity [34].

$$D_{ij}^o = \left(\frac{117.3\mathrm{E}-18(\varphi \times MW_j)^{0.5}T}{\mu \upsilon_i^{0.6}} \right) \tag{22}$$

where D_{ij}^o, MW, T, φ, μ and υ are diffusivity of component i in very dilute solution in solvent j (m^2/s), molecular weight, temperature (in K), association factor for solvent, solution viscosity (kg/m·s) and solute molal volume at normal boiling point (m^3/kmol), respectively. However, the diffusivity in concentrated solutions differs from that in dilute solutions because of changes in viscosity with concentration (x_i) [35,36] and also because of changes in the degree of non-ideality of the solution (γ_i) [34].

Table 5. Experimental and predicted values of some physical properties

Objective function	Molecular weight	Vapor pressure at 398.3 °C (atm)	Kinematic viscosity at 40 °C (cSt)	Kinematic viscosity at 100 °C (cSt)	Refractive index at 20 °C	Refractive index at 40 °C	MeABP ($\approx T_{50}$, °C)
Experimental data[a]	**304.23**	**1.00**	**32.19**	**4.93**	**1.5058**	**1.4978**	**398.30**
Molecular weight (MW)	304.81	1.31	29.89	4.42	1.5073	1.4993	382.15
Pressure-VP[b] - ideal	320.18	1.00	48.26	5.75	1.5109	1.5029	397.85
Pressure-PP[c] - ideal	323.57	1.00	50.99	5.94	1.5115	1.5035	397.85
Pressure-VP- non ideal	320.71	0.99	48.58	5.77	1.5109	1.5029	399.23
Pressure-PP- non ideal	323.68	1.00	50.09	5.89	1.5113	1.5033	398.85
Pressure+ MW-VP- ideal	303.26	1.31	34.74	4.73	1.5081	1.5001	382.15
Pressure+ MW-PP- ideal	308.65	1.27	37.36	4.96	1.5086	1.5006	384.76
Pressure+ MW-VP- non ideal	303.26	1.31	34.74	4.73	1.5081	1.5001	382.15
Pressure+ MW-PP- non ideal	308.60	1.27	37.32	4.95	1.5086	1.5006	384.76
Kinematic viscosity	338.04	0.93	32.19	4.93	1.5077	1.4997	401.88
Watson K factor	308.92	1.22	32.82	4.67	1.5078	1.4998	386.65

[a]Reported by Vakili-Nezhaad et al. [16]
[b]VP: vapor pressure constraint
[c]PP: partial pressure constraint

$$D_{ij}\mu_{mix} = (D_{ji}^o\mu_i)^{x_i}(D_{ij}^o\mu_j)^{x_j}\left(1+\frac{d\log(\gamma_i)}{d\log(x_i)}\right) \quad (23)$$

where D_{ij}^o is the diffusivity of component i at infinite dilution in j and D_{ji}^o the diffusivity of component j at infinite dilution in i. Also, the entire two-phase mass transfer effect (as a result of diffusive and forced convective movements) can be measured in terms of overall liquid mass transfer coefficient (K_x), where m, k_x and k_y are the slope of specific chord on equilibrium curve (dimensionless) and local mass transfer coefficients (kmol/(m²·s·mole fraction)) [34].

$$K_x = \left(\frac{k_x + mk_y}{mk_yk_x}\right)^{-1} \quad (24)$$

The local mass transfer coefficients can also be related to diffusion coefficient through Sherwood number as follows, where Sh and C are Sherwood number and molar concentration, and x_{jM} and y_{jM} are the natural logarithmic average of the concentration of component j.

$$k_x = \left(\frac{Sh \times CD_{ij}}{x_{jM}L}\right) \quad (25)$$

$$k_y = \left(\frac{Sh \times CD_{ij}}{y_{jM}L}\right) \quad (26)$$

Diffusivity thus plays a prominent role in both the diffusive and convective mass transfer phenomena as it is clear from Eqs. (22) to (26). Also, as shown in Eqs. (22) and (23), diffusivity is proportional to the first power of the inverse viscosity, but it depends on MW to the power 0.5. Therefore, it is expected that the viscosity adjusting leads to a more accurate modeling of mass transfer phenomena, in comparison with other physical properties (e.g., MW or vapor pressure). For example, in absence of any LLE data on lube-oil cut SAE 10 from Tehran oil refinery, a comparison was done between viscosity approach and prior methods through LLE data for five pseudo-quinary systems composed of blend naphtha (consisting of P, N and A species), sulfolane and water as shown in Table 6. The comparisons between the experimental and calculated composition of each component in each of the two phases were made through root mean square deviation (RMSD), given by:

$$RMSD = 100\sqrt{\frac{\sum_i^M\sum_j^C((w_{ij}^{I,exp.} - w_{ij}^{I,cal.})^2 + (w_{ij}^{II,exp.} - w_{ij}^{II,cal.})^2)}{2MC}} \quad (27)$$

where C and M are the number of components and tie-lines in each data set, respectively. It is clear that, despite the simplicity, the viscosity approach leads to a more accurate prediction of composi-

tions of both phases.

Also, as mentioned above, n_D is a very sensitive factor, especially in relation to structural groups and composition [11,24] and it varies in a fairly narrow range. Therefore, a slight improvement in its estimation can represent a prominent improvement in the molecule structure and consequently a more accurate modeling of LLE.

CONCLUSIONS

Two procedures were developed to determine representative molecules of petroleum fractions based on bulk properties. Ruzicka's structural models were used to model lube-oil cut as a case study for validation of the proposed methodology. Unlike previous studies, the main emphasis in the present research was on the structural modeling of petroleum fractions using minimum and easily measurable laboratory data (viscosity, density and refractive index). There is reasonable agreement between the measured and predicted data. Due to simplicity, the new procedures take less run-time and can be reliably extrapolated for a wide range of hydrocarbon mixtures. Unlike Ruzicka's procedure, the new approaches provided higher a degree of accuracy for medium and heavy fractions because of their non-ideality consideration. In addition, we found that the application of the vapor pressure constraint is preferred over the reported partial pressure constraint in structural modeling of light hydrocarbons through Ruzicka's procedure.

NOMENCLATURE

Symbols

A_i, B_i, C_i, D_i : compound-class coefficients of MW distribution functions

B_{m0}, B_{m1} : compound class coefficients (Table 1)

C : number of components in each LLE data set

COH : carbon to hydrogen weight ratio

d : liquid density [g/cm³]

D_{ij} : diffusivity or diffusion coefficient [m²/s]

ECN : effective carbon number

I : Huang's factor

k_x and k_y : local mass transfer coefficients [kmol/(m²·s·mole fraction)]

K_w : watson (UOP) K factor

K_x : overall liquid mass transfer coefficient [kmol/(m²·s·mole fraction)]

m : slope of specific chord on equilibrium curve [dimensionless]

M : number of tie-lines in each LLE data set

MW : molecular weight [g/mol]

n : parameter of the structural model (Fig. 1)

Table 6. UNIFAC correlation results for LLE prediction through different approaches

Feed mass composition					Temperature (°C)	RMSD (%)		
w_P	w_N	w_A	w_{H2O}	$w_{Sulf.}$		Pressure approach	MW approach	Viscosity approach
0.142	0.053	0.023	0.016	0.767	54	1.75	1.58	1.51
0.217	0.081	0.035	0.033	0.633	45	1.58	1.67	1.50
0.163	0.061	0.026	0.037	0.712	60	0.89	0.95	0.82
0.192	0.072	0.031	0.014	0.692	54	1.30	1.31	1.15
0.130	0.049	0.021	0.040	0.760	45	0.93	0.88	0.72

N_C : carbon number
n_D^T : sodium D line refractive index of liquid at T (in K) and 1 atm
P : vapor pressure of the real mixture [atm]
P_i^0 : vapor pressure of i-th compound of the model mixture [atm]
R_m : molar refraction defined in Eq. (14) [cm^3/mol]
RI : refractivity intercept (defined in Fig. 2)
SG : specific gravity
Sh : Sherwood number [dimensionless]
T : temperature [K]
T_B : boiling point temperature [K]
THC : total hydrogen content
W_i : MW distribution function of i-th hydrocarbon group
w_i : weight fraction
x_i : mole fraction of i-th compound of the model mixture
x_{jM} : natural logarithmic average of the mole fraction of component j

Greek Symbols

α : parameter of the structural model (Fig. 1)
β : parameter of the structural model (Fig. 1)
γ : cctivity coefficient
μ : Dynamic viscosity [mPa·s]
v_T : kinematic viscosity at temperature T [mm^2/s]
σ^2 : variance
φ : association factor for solvent [dimensionless]
υ : solute molal volume at normal boiling point [m^3/kmol]

Abbreviations

A : aromatic hydrocarbons
AMP : abrams-Massaldi-Prausnitz group contribution method
LLE : liquid-liquid equilibrium
MeABP : mean average boiling point
N : naphthenic hydrocarbons
NRCT : normalized required computation time
OF : objective function
P : paraffinic hydrocarbons
RMSD : root mean square deviation
ROd : ratio of densities (Fig. 2)
ROI : ratio of Huang's factors (Fig. 2)
SM : structural modeling
TBP : true boiling point

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