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Characterization of petroleum fractions

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ABSTRACT:

Petroleum streams produced from distillation of crude oil such as gasoline, kerosene, diesel fuel, fuel oil, etc. are complex mixtures of large numbers of hydrocarbon components, such fractions are generally characterized in terms of small petroleum cuts, or pseudocomponents, which are identified primarily by their boiling point and specific gravity due to their true boiling point curve (TBP), based on these two properties empirical correlations were derived to predict other components physical properties required for the process calculations. In the present paper empirical correlations was compared to other correlated equation and gives a good agreement. The proposed model is very interest for vapor-liquid equilibrium calculations of complex mixtures.

خصائص القطفات النفطية

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الخلاصة

القطفات النفطِيةِ الناتجة مِنْ عملية تكرير النَفط الخامِّ مثل الغازولينِ، نفط أبيض، وقود الديزل، زيت الوقود، الخ. خلطاتَ معقّدةَ مِنْ اعداد كبيرةِ مِنْ مكوّناتِ هيدروكربونِ، عموما يعبر عن مثل هذه المنتجات بشكل مقاطع صغيرة او مركبات وهمية تعرف على اساس درجةِ غليانها ووزنها النوعي الناتجة من منحنى درجةِ غليانهم الحقيقي . تم اشتقاق معادلات إرتباطِ تجريبيةِ إستناداً الى الخاصيتين اعلاه لحساب الخصائص الفيزيائية الاخرى اللازمة لأجراء العمليات الحسابية من موازنة الطاقة والكتلة وغيرها. تم مقارنة المعادلات المقترحة مع مع علاقات تجريبية أخرى وقد اعطت توافق جيد. إنّ النموذجَ المُقتَرَحَ مفيد جداً ُ لحساباتِ توازنِ البخارِ- السائل للخلطاتِ المعقّدةِ.

There is great deal of interest in the petroleum and natural gas industries to develop computational packages to predict the behavior of such mixtures(6).

The presented work is an attempt to predict physical properties of such mixtures due to interested data.

In this context, we consider a mixture "complex" when its discrete light-component impurities and hydrocarbons (up to a certain carbon number) can be individually identified and characterization of its heavy hydrocarbons called "plus-fraction" are specified. The major obstacle in the efficient design of processes dealing with hydrocarbon mixtures is the difficulty in the accurate and efficient prediction of physical properties. This is because for many naturally occurring hydrocarbon mixtures complete compositional analysis is not available. As a result, one can not utilize the existing industrial packages in which identification of all the real and pseudo-components are necessary. Also, in cases where the complete compositional analysis is available, the computational schemes become quite lengthy (5) and inefficient due to the lack of the related pure components characterization parameters and properties. To overcome this difficulty there exist at least two approaches in the literature:

(i) In the first approach which is usually called “the pseudo-component approach” a mixture is divided into known light components and several plus-fractions, with arbitrary parts, consisting of several neighboring species(7). By using the pseudocomponent method for petroleum fluids, the lighter components (for example C1 to C6) are analytically identified and the heavier parts (in this case C7+ fractions) are empirically split into a number of fractions that each is characterized by one or more average properties. On the other hand, some highly complex petroleum fluids contain various families of compounds such as paraffinic, olefinic, naphtenic and aromatic hydrocarbons for which application of the pseudocomponent method would require specification of a very large number of pseudo-components. Thus, accurate phase equilibrium calculation of such complex mixtures by using this approach would demand a great deal of computer time. In addition, the method of selecting the pseudocomponents and calculation of their compositions and properties is quite sensitive on the results of the calculations (7) .

CHARACTERIZING PETROLEUM FRACTIONS:

Petroleum streams—from crude oil to products such as gasoline, kerosene, diesel fuel, fuel oil, etc.—are mixtures of large numbers of hydrocarbon components. It is impractical to analyze such mixtures and represent them compositionally based on their constituent components. Petroleum streams are generally characterized in terms of small petroleum cuts, or pseudocomponents, which are generated from their distillation curves. The pseudocomponents are identified primarily by their boiling point and specific gravity, and these two properties may be used to predict other component properties required for process calculations.

True Boiling Point:

In a perfect batch distillation process where a sharp separation of the components in a mixture occurs, a distillation curve can be represented by a number of steps equal to the number of components in the mixture (Figure 1.18). The boiling point at a given pressure (usually atmospheric) is plotted against the fraction distilled, usually on a volume basis. If, for instance, the mixture contains four components, the distillation curve would include four steps showing the boiling points and volumes of the components:

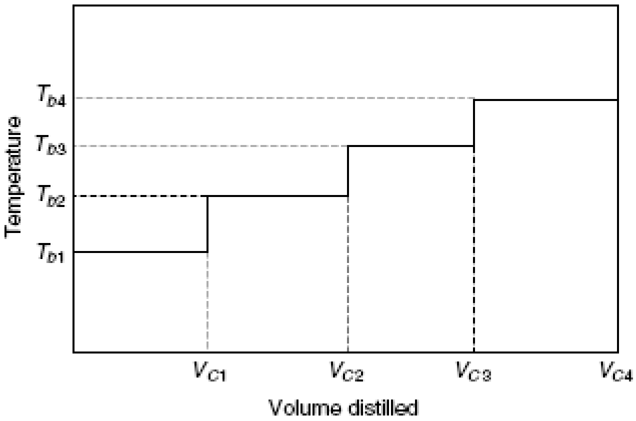


FIGURE 1.18 True boiling point curve of a mixture with a limited number of components.

Component 1 is of volume V_{C1} with boiling point T_{b1}; component 2 of volume $V_{C2} - V_{C1}$ with boiling point T_{b2}; and so on. The distillation curve of a petroleum mixture containing a large number of components would consist of many small steps. Since the separation can only approach perfect fractionation, and because of the large number of components in a complex mixture, the steps in the distillation curve or true boiling point (TBP) curve of a petroleum mixture tend to merge into a smooth curve as shown in Figure 1.19.

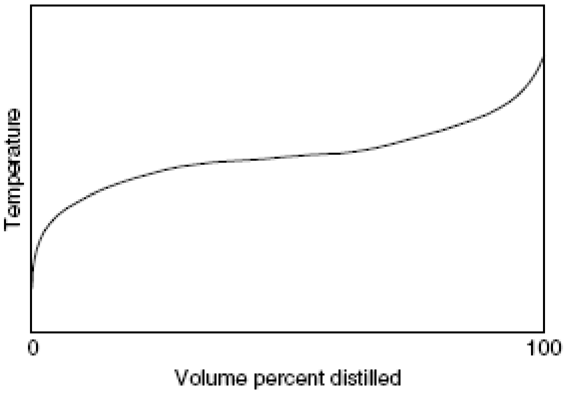


FIGURE 1.19 True boiling point curve of a petroleum mixture

Generating Pseudocomponents:

If a petroleum mixture is represented by pseudocomponents corresponding to its TBP curve, its properties can be estimated by the same methods that apply to mixtures of chemical species. For instance, the mixture enthalpy and phase behavior can be predicted by the methods discussed in this chapter. Generating the pseudocomponents from a TBP curve is accomplished by breaking the curve into a number of cuts as shown in Figure 1.20. Temperatures T_{C1}, T_{C2}, T_{C3}, … , define the cut points. Thus, the first pseudocomponent boiling range is from the initial boiling point of the mixture to T_{C1}, the second pseudocomponent from T_{C1} to T_{C2}, etc. The number of cut points determines the number of pseudocomponents generated. The higher this number, the more accurately these pseudocomponents can reproduce the original TBP curve and represent the mixture. There are practical upper limits on the number of components, such as their effect on computing time in computer simulation. The spacing of the cut points does not necessarily have to be constant. It may be advantageous to define more cuts where the separation of the mixture is expected to take place, as more cuts would help produce a sharper separation.

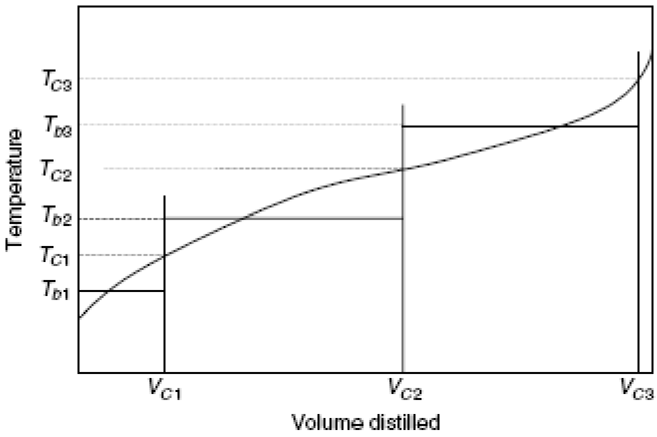


FIGURE 1.20 Generating pseudocomponents from a TBP curve

The volume cut points correspond to the temperature cut points on the TBP curve: T_{C1} defines V_{C1}; T_{C2} defines V_{C2}, … (Figure 1.20). The boiling point T_{bi} of pseudocomponent i is calculated as an average:

$$T_{bi} = \frac{\int_{V_{C,i-1}}^{V_{Ci}} T dV}{V_{Ci} - V_{C,i-1}}$$

If T, the TBP temperature, can be expressed as a mathematical function of V, the integral may be evaluated analytically. More commonly, the integration is done based on some sort of curve fitting technique. Once the pseudocomponents are generated, their properties are estimated from correlations that are functions of the components' boiling points and specific gravities.

Laboratory Data:

True boiling point curves are not usually determined directly by batch distillation because achieving complete fractionation in the laboratory is impractical. Instead, standardized batch distillation tests are conducted under closely defined conditions. Several such tests are specified by the American Society for Testing and Materials, including procedures D86, D1160, and D2887 (ASTM, 1990). These

distillation curves are converted to TBP curves using methods documented by the American
Petroleum Institute (API, 1983).

The specific gravity may either be measured as an average or overall gravity of the mixture, or as discrete values of cuts obtained in the batch distillation test. In the latter case the specific gravity of the cuts are measured and plotted against the volume percent distilled. This gravity curve is used to determine the pseudocomponent gravities in a manner similar to the method used for determining the pseudocomponent boiling points. If only the average specific gravity of the mixture is available, the individual pseudocomponent gravities can be estimated. One method involves the Watson characterization factor, *KW*, defined as:

$KW = (Tba)1/3/S$

Where *Tba* is an average boiling point of a pseudocomponent or of the mixture, in degrees Rankine, and *S* is the specific gravity of the pseudocomponent or the mixture. The method is based on the assumption that, over reasonable ranges of boiling points, *KW* is almost constant for a mixture and the cuts derived from it. The average boiling point of the mixture is calculated from its distillation curve (API, 1983). With known average boiling point and gravity, the mixture *KW* can be calculated, and the pseudocomponent gravities are calculated from the above equation using their individual average boiling points. The calculated pseudocomponent gravities may have to be normalized in order to force their composite specific gravity to match the measured mixture-specific gravity.

Pseudocomponent Properties:

Stream properties required for solving material and energy balance equations and other process calculations are predicted from component properties. The properties of petroleum pseudocomponents can be estimated from their boiling points and specific gravities. The component properties include the molecular weight, critical constants, acentric factor, heat of formation, ideal gas enthalpy,
latent heat, vapor pressure, and transport properties. These are predicted mainly by empirical correlations based on experimental data. Many of these correlations are documented in the American Petroleum Institute Technical Data Book (API, 1983).

2. Crude Oil Assay

A crude oil assay always includes a whole crude API gravity and true boiling point (TBP) distillation curve at atmospheric pressure. The characteristics of the vapors and liquids formed when a complex mixture is flashed under equilibrium conditions may be estimated in a number of ways, essentially the various methods involve the arbitrary breakup of the mixture into cuts representing pseudo-components. This is accomplished by carrying out the following distillation types.

2.1 TBP Distillation:

The composition of the crude oil usually, is approximated as measured by True Boiling Point (TBP) distillation, this method is basically a batch distillation using number of stages and a high reflux ratio. They are normally running only on crude oil as well as on petroleum fractions under atmospheric or vacuum pressure to determine the boiling range of petroleum fractions. The actual boiling point can be shown on a TBP curve, which is one of the most important test of a crude assay in which the percentage distilled or recovered is plotted against the temperature at which it's distilled as shown in Fig.(1). The composition of whole crude can be obtained based on dividing the TBP curve into a series of narrow boiling cuts or fractions; each characterized by its mean average boiling point, and its represented by an individual component, the number of pseudo-components in each breakdown is arbitrary. However, greater accuracy can be obtained by using more components of narrower width. Usually, the composition given as a volume percent or weight percent and should be converted to a molar percent as follows :

$$x_i = \frac{x_{vi}\rho_i / Mw_i}{\sum_{k=1}^{m} x_{vk}\rho_k / Mw_k} \quad \text{or} \quad x_i = \frac{x_{wi} / Mw_i}{\sum_{k=1}^{m} x_{wk} / Mw_k} \qquad (1)$$

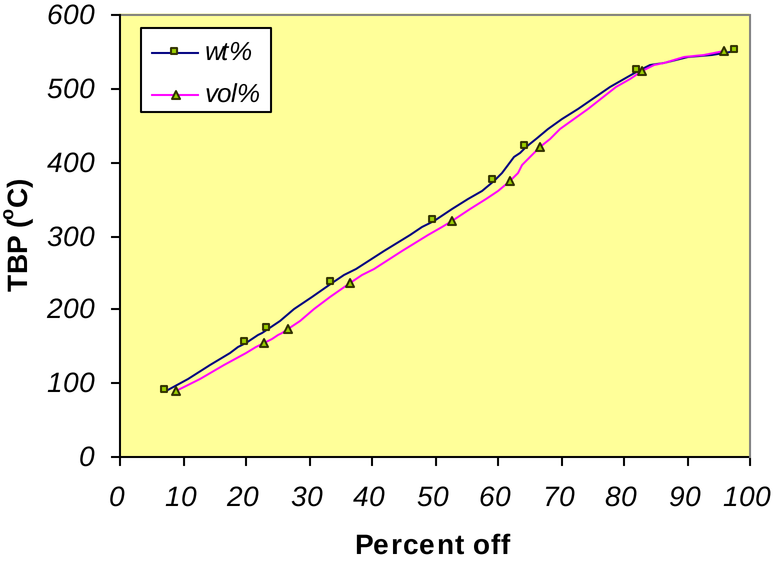


Fig.(1) True boiling point distillation curve.

2.2 ASTM Distillation:

The American Society for Testing Materials (ASTM) distillations are developed procedures of the TBP distillation. There are many different types of ASTM distillation methods for testing of petroleum fractions ,such as D58, D216, D158 and D1160. These methods are rapid batch distillations employing no trays, packing or reflux between the still pot and condenser. The only reflux available is that generated by the heat losses from the apparatus. In the ASTM there may be residue left in the distillation equipment, which is the difference between the volume of the original charge and the sum of the distillate and residue, this difference is usually termed "loss" as is generally thought as volatile components of the charge which have not been re condensed.

The temperature of the vapor when the first drop is vaporized as the initial point (I.P) . When 95 percent has been distilled, the burner flame may need to be increased, and the maximum temperature is recorded as the end point (E.P). Both ASTM and TBP distillation are used to define the volatility characteristics of petroleum fractions and other complex mixtures, but they differ mainly in the degree of fractionation obtained during the operation (9).

Virtually no fractionation occurs in this distillation, and the hydrocarbons in the oil do not distill one by one in the order of their boiling points, but as successively cuts having higher boiling ranges. Actually the initial boiling point, the end point, and the intermediate vapor temperatures have little significance except when compared with corresponding points from other ASTM distillations. Materials boiling below the initial boiling point and above the end point are present in the oil, although these points are the extreme ends of the ASTM distillation range. The ASTM curve for different fractions as shown in Fig.(2).

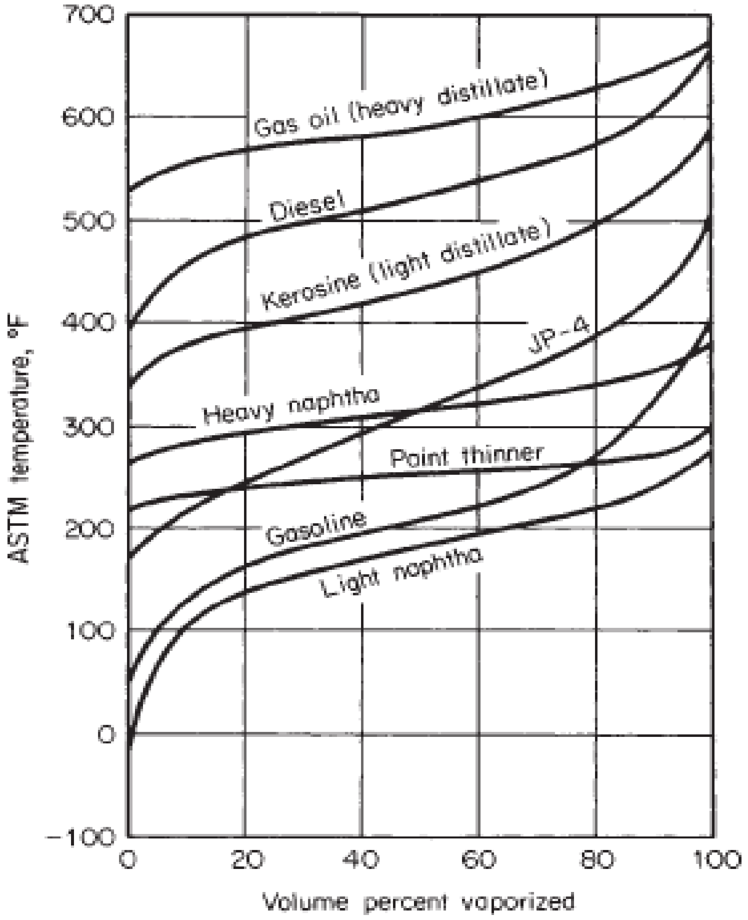


Fig. (2) Representative ASTM D86 distillation curves.

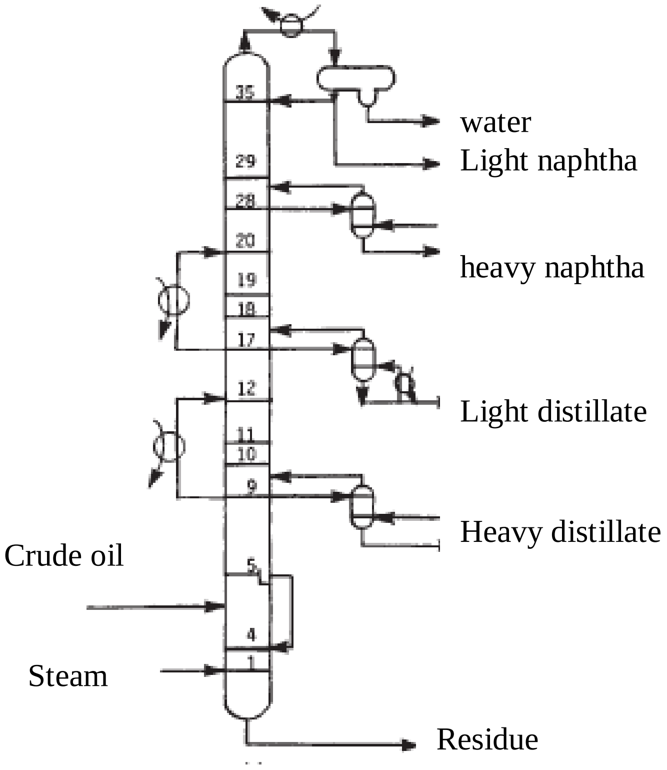


Fig. (3) Atmospheric distillation unit of crude oil.

3. Category of Petroleum Fractions

Most petroleum distillates, especially these from atmospheric distillation tower shown in Fig.(3), have different physical properties depending on the characteristics of the crude oil feeding. The content of different distillates will vary from refinery to another. Usually the petroleum fractions are defined in term of an ASTM boiling point range and API gravity, the crude oil assay and general classes of distillate products are obtained from crude oil under atmospheric pressure are summarized in Table 1.

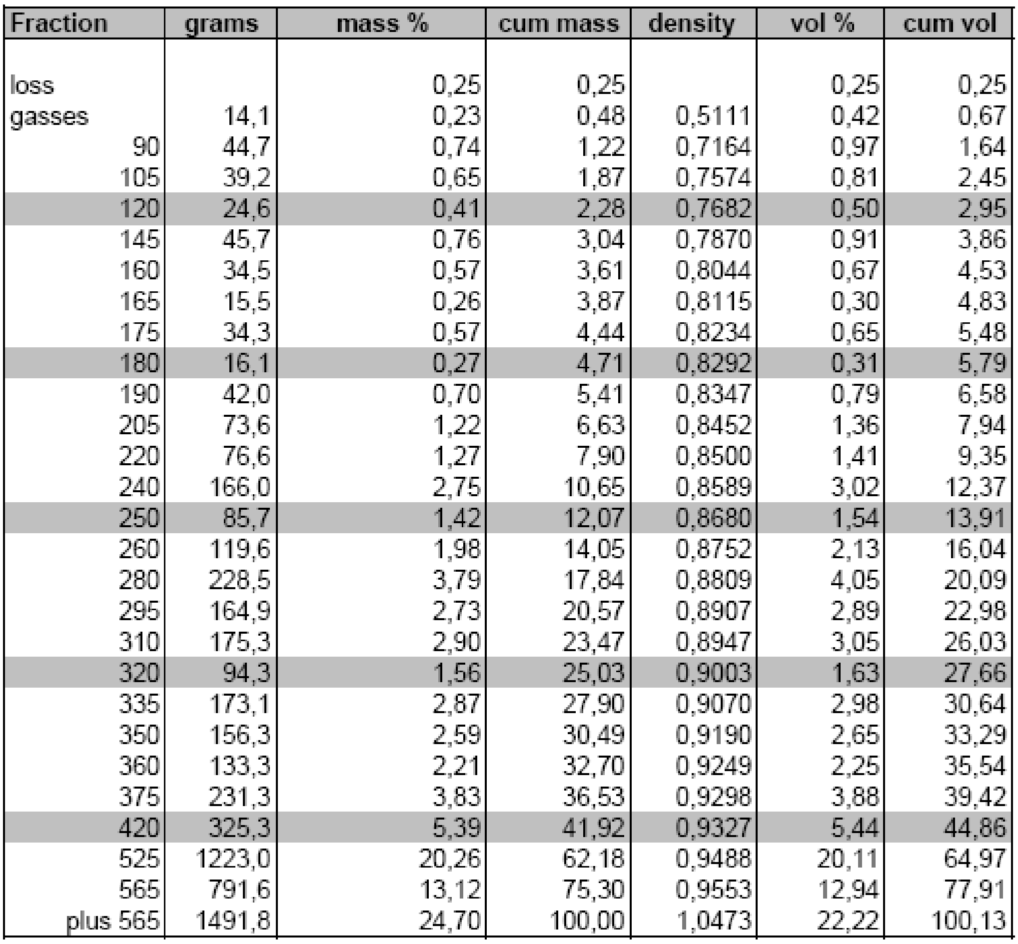
Table (1) properties of petroleum fractions.

petroleum fractions	boiling point (^{o}C)	average specific gravity	Number of C atoms	apparatus	uses
L.P.G	Up to 30	0.6	1 to 4	ASTM D86	Camping stoves
Light naphtha	30 to 100	0.69	5 to 8	ASTM D86	Fuel for cars
Heavy naphtha	100 to 150	0.758	8 to 10	ASTM D86	Reforming petrochemical feed
Kerosene	150 to 250	0.808	10 to 14	ASTM D86	Fuel for aero plane
Light gas oil	250 to 350	0.84	15 to 20	ASTM D216	Fuel for lorries, train and cars

Heavy gas oil	350 to 450	0.885	21 to 28	ASTMD158	Lubricant heating
Residue	over 450	0.945	over 28	ASTMD1160	roads surfacing

The true boiling point and density data of whole crude are listed in Table (3).

Table (3) boiling point and density data of whole crude



Fraction	grams	mass %	cum mass	density	vol %	cum vol
loss		0,25	0,25		0,25	0,25
gasses	14,1	0,23	0,48	0,5111	0,42	0,67
90	44,7	0,74	1,22	0,7164	0,97	1,64
105	39,2	0,65	1,87	0,7574	0,81	2,45
120	24,6	0,41	2,28	0,7682	0,50	2,95
145	45,7	0,76	3,04	0,7870	0,91	3,86
160	34,5	0,57	3,61	0,8044	0,67	4,53
165	15,5	0,26	3,87	0,8115	0,30	4,83
175	34,3	0,57	4,44	0,8234	0,65	5,48
180	16,1	0,27	4,71	0,8292	0,31	5,79
190	42,0	0,70	5,41	0,8347	0,79	6,58
205	73,6	1,22	6,63	0,8452	1,36	7,94
220	76,6	1,27	7,90	0,8500	1,41	9,35
240	166,0	2,75	10,65	0,8589	3,02	12,37
250	85,7	1,42	12,07	0,8680	1,54	13,91
260	119,6	1,98	14,05	0,8752	2,13	16,04
280	228,5	3,79	17,84	0,8809	4,05	20,09
295	164,9	2,73	20,57	0,8907	2,89	22,98
310	175,3	2,90	23,47	0,8947	3,05	26,03
320	94,3	1,56	25,03	0,9003	1,63	27,66
335	173,1	2,87	27,90	0,9070	2,98	30,64
350	156,3	2,59	30,49	0,9190	2,65	33,29
360	133,3	2,21	32,70	0,9249	2,25	35,54
375	231,3	3,83	36,53	0,9298	3,88	39,42
420	325,3	5,39	41,92	0,9327	5,44	44,86
525	1223,0	20,26	62,18	0,9488	20,11	64,97
565	791,6	13,12	75,30	0,9553	12,94	77,91
plus 565	1491,8	24,70	100,00	1,0473	22,22	100,13

4. Characterization of petroleum fraction

The properties of undefined hydrocarbon mixture are usually characterized by parameters that are derived from normal inspection tests, an ASTM D86 or D1160 distillation, and the specific gravity of the mixture.

Gravity of a crude-oil or petroleum fraction is generally measured by the ASTM D287 test or the equivalent ASTM D1298 test and may be reported as specific gravity (S) 60/60°F [measured at 60°F (15.6°C) and referred to water at 60°F, more commonly, as API gravity, which is defined as

$$API\ \ gravity = \frac{141.5}{S} - 131.5 \qquad (2)$$

Most crude oils and petroleum fractions have values of API gravity in the range of 10 to 80. Light hydrocarbons (*n*-pentane and lighter) have values of API gravity ranging upward from 9 to 28.

Although much progress has been made in identifying the chemical species present in petroleum, it is generally sufficient for purposes of design and analysis of plant operation of distillation to characterize petroleum and petroleum fractions by gravity, laboratory-distillation curves, component analysis of light ends, and hydrocarbon-type analysis of middle and heavy ends. From such data(1), five different average boiling points and an index of paraffinicity (Watson characterization factor) can be determined (11,12); these are then used to predict the physical properties of complex mixtures by a number of well-accepted correlations.

Volumetric average boiling point

$$VABP = \sum_{i=1}^{m} x_{vi} T_{bi} \tag{3}$$

Where x_{vi} volume fraction of component i, and T_{bi} normal boiling point of component i, either Fahrenheit or Rankine units may be used for volumetric average boiling point, molal average boiling point, and weight average boiling point to give the same units for the average boiling point. Rankine units must be used for cubic average boiling point, however, the MABP and CABP must be in the same units to calculate mean average boiling point.

Molal average boiling point

$$MABP = \sum_{i=1}^{m} x_i T_{bi} \tag{4}$$

Weight average boiling point

$$WABP = \sum_{i=1}^{m} x_{wi} T_{bi} \tag{5}$$

Cubic average boling point

$$CABP = \left(\sum_{i=1}^{m} x_{vi} T_{bi}^{1/3} \right)^3 \tag{6}$$

Mean average boiling point:

which is the arithmetic average of the molal boiling point and the cubic volumetric average boiling point

$$MeABP = \frac{CABP + MABP}{2} \tag{7}$$

characterization factor

The ASTM D2892 test method includes a correction for the nature of the sample (paraffin, olefin, napthene, and aromatic content) in terms of the UOP characterization factor K , as given by (1).

$$K = \frac{\sqrt[3]{MeABP}}{S} \tag{8}$$

Where *MeAB* is the mean average boiling point in degrees Rankine and S is the specific gravity at 15°C. The Watson K is an approximate index of paraffinicity (the higher value of K the higher degree of saturation).

5. **Correlations of Physical Properties:**

The physical properties of undefined hydrocarbon mixtures are calculated as functions of the true boiling point and specific gravity of petroleum cuts, depending on collection data, the empirical equation was suggested for the presented work as follow:

$$\theta = k \times EXP(aT + bS) \qquad (9)$$

where θ is a physical property to be predicted, T is a dimensionless boiling point temperature and S is a specific gravity and this technique is used to avoide the undefined quantity or over flow numbers. *k*, *a*, and *b* are correlation constants of eq. (9) which are predicted and tabulated in Table 3. The prediction accuracy is reasonable over the boiling range of 100-850 °F (38-455 °C) for the following properties: molecular weight, liquid density, liquid molar volume, critical temperature, critical pressure, critical volume, and heat of vaporization. The experimental data were taken from (10).

Table(3) correlation coefficients for presented empirical equation.

property	k	a	b
Mw	13.03251	0.81348	1.332426
T_c	60. 7002	0.2613213	2.4851934
P_c	1164.2722	-0. 87345	0.26911
V_c	0.0881418	0.115785	-0.67066
V_m	44.26796	0.799526	0.106324
λ	2755.825	0.412988	1.4198218
ρ	0.2751615	-0.012786	1.347846

Equation 9 should be by linearized as below

$$\ln\theta = \ln k + aT + bS \qquad (10)$$

The computer program in a visual basic are designed to determine the correlation coefficients k, a,and b from the regression analysis . Table (3) give the results of the fitting method.

Equation of state :

In order to perform bulk property and phase equilibrium calculation for a petroleum fluid at various conditions of temperature and pressure, we need to use equations of state. Parameters of majority of equations of state for a fluid mixture are expressed with respect to the critical properties, acentric factor, unlike interaction parameters, and compositions of components of the mixture under consideration. For the plus-fraction of a petroleum fluid mixture, narrow range fractions can be assumed as discrete pseudo-components. In order to determine parameters of the equation of state, the true boiling point of the plus-fraction cuts are necessary.

6. Results and Discussion:

Figs. (4-9) show the comparison between the results due to experimental values correlated by Riazi and Daubert [(8)] and the present correlation represented by Eq.9 for different properties of petroleum fractions (psedo-components). Each figure have fitting of the data and the linear equation represent the relation between the two works, slope and the intersect constants. All data points are lie and distributed rounded the straight line which passes through it and gives indicator for the validity of the presented model.

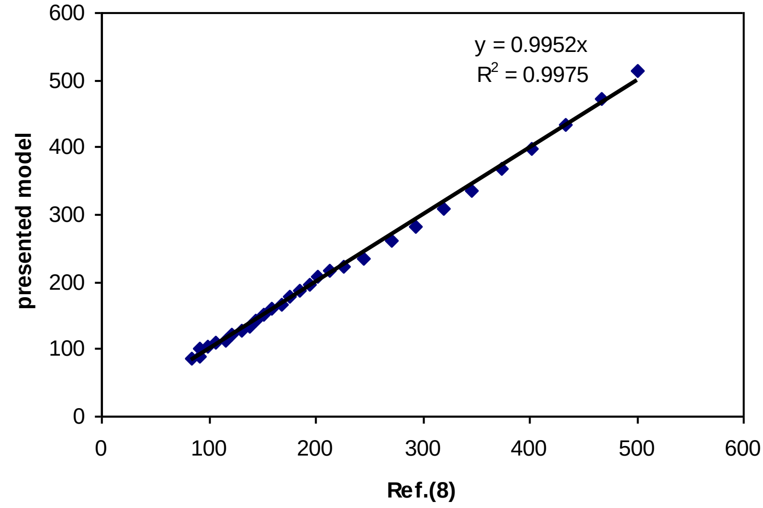


Fig.(4) Comparison of molecular weight (kg/kmole) of petroleum fractions for presented model and Riazi & Daubert(8).

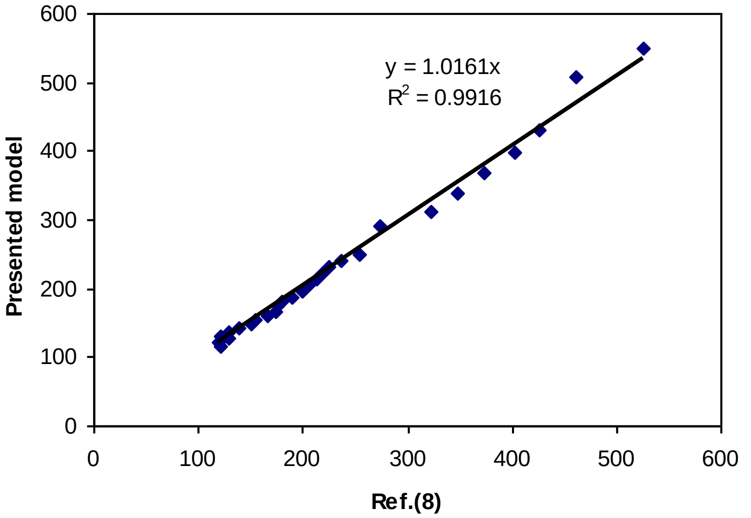


Fig.(5) Molar volume of petroleum fractions (cft/lbmole)

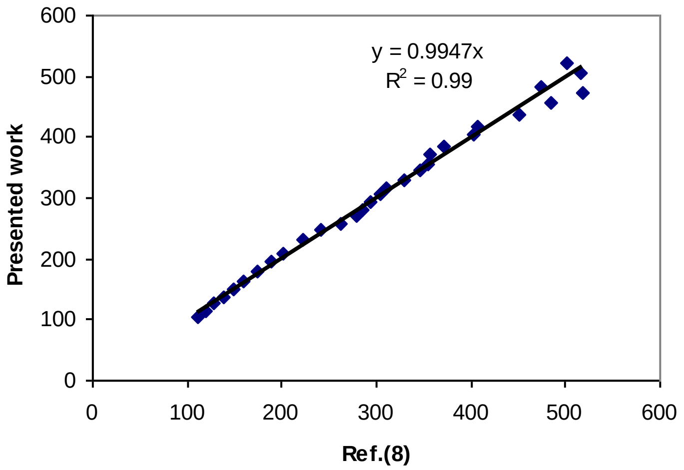


Fig.(6) Critical pressure of petroleum fractions (psia).

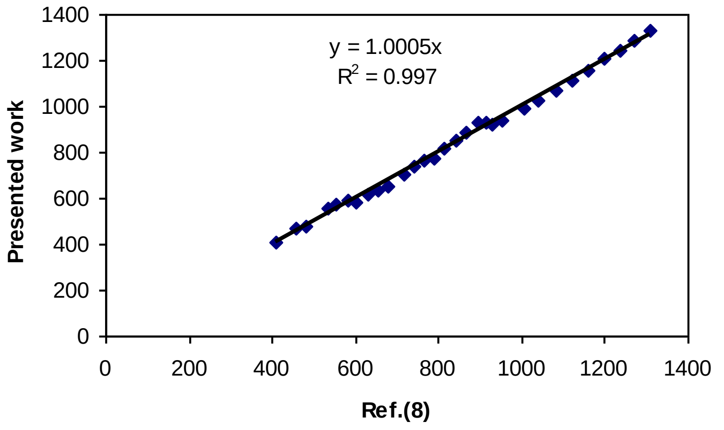


Fig.(7) Latent heat of vapourization of petroleum fractions (Btu/lbmole).

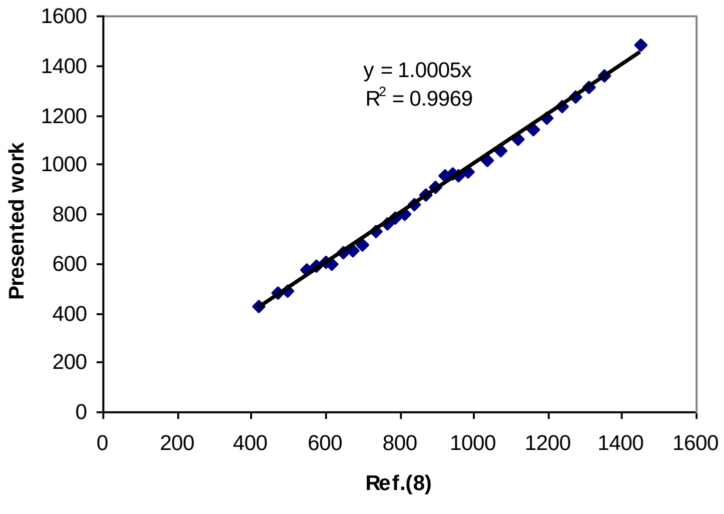


Fig.(8) Density of petroleum fractions (kg/m^3).

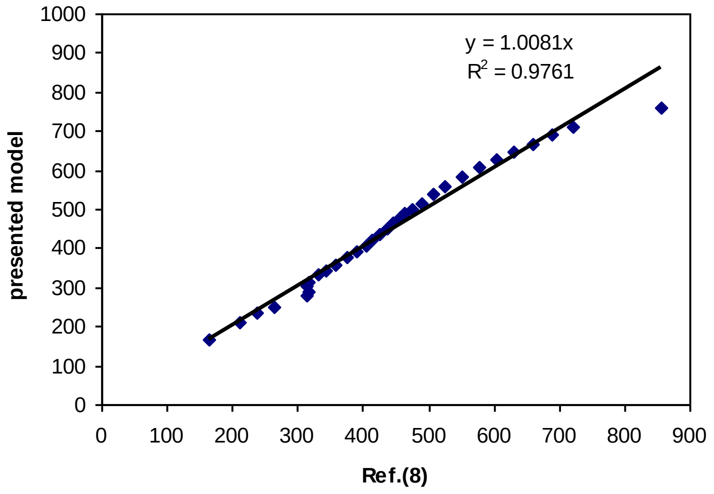


Fig.(9) Critical temperature (^{o}F) of petroleum fractions.

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Nomenclatures:

K	characterization factor
Mw	molecular weight (kg/kgmole)
S	Specific gravity
P	pressure (N/m^2)
T	temperature (K)
T_b	True boiling point®
V	volume (m^3)
V_m	Molar volume(m^3/kgmole)
x	mole fraction of discrete components

Greek letter

ρ	density (kg/m^3)
λ	latent heat of vaporization (Cal/kgmole)

subscript

c	critical property
m	molar
r	reduced property
v	volumetric
w	weight