CALCULATION OF VOLUMETERIC AND THERMODYNAMIC PROPERTIES FOR PURE HYDROCARBONS AND THEIR MIXTURES USING CUBIC EQUATIONS OF STATE

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ABSTRACT

The objective of this study was to develop a complete package for prediction of volumetric and thermodynamic properties of pure hydrocarbons fluids and their mixtures in one and two phase regions. Two cubic equations of state that are Peng-Robinson and Soave-Redlich-Kwong were used with volatile and black oils respectively to calculate the desired properties in addition to bubble point and dew point pressures and temperatures. Different values of binary interaction parameter were used for each equation and effects of this parameter values on the prediction are examined. Also values of this parameter between the plus-fraction and other component have been evaluated for first time. In calculation of heat capacity, four different mixing rules have been proposed to evaluate the temperature derivatives in case of the mixtures. Wide comparisons with the literature experimental data were made which indicated that both equations of state predict accurately different properties and marked improvements are achieved by use binary interaction parameter other than zero. Also both equations predict bubble point pressure of a certain mixture approximately with same accuracies using the recommended values of binary interaction parameter. Among the proposed mixing rules, Kay’s one appeared the best one to determine temperature derivatives.

الخلاصة

كان الهدف من هذه الدراسة هو تطوير برنامج متكامل لتنبؤ بالخواص الفيزيائية والثرموديناميكية للمركبات الهيدروكاربونية وخلائطها في طوري الغاز والسائل. تم استخدام معادلتين من معادلات الحالة وهما بنك-روبنسن وسواف-ريدلك-ونك لنفوط الخفيفة والثقيلة على التوالي لحساب الخواص المطلوبة وكذالك ضغوط ودرجات الحرارة لنقطة الفقاعة ونقطة الندى. لدراسة تاثير معامل التداخل الثنائي على الحسابات استخدمت مع PR Eos اربعة مجاميع مختلفة من معامل التداخل الثنائي و مجموعتين مع SRK Eos. ولاول مرة تم في هذه الدراسة حساب قيم هذا المعامل بين Plus Fraction وبقية المركبات كما اقترح ايضا استخدام المجموعة الرابعة المستخدمة مع PR Eos مع معادلة SRK. لحساب السعة الحرارية النوعية, تم اقتراح اربعة قواعد للمزج لتقيم مشتقات الحرارة في حالة الخلائط. مقارنات واسعة مع القيم التجريبية المنشورة في الادبيات تمت واعطت مؤشرا ان هاتين المعادلتين تتنبا بمختلف الخواص بدقة عالية وتحسينات ملحوظة تحققت باستخدام قيم لمعامل التداخل الثنائي غير الصفر. كذالك كلا المعادلتين وجدتا ضغط الفقاعة لمزيج معين تقريبا بنفس الدقة عند استخدام قيم معامل التداخل الموصى بها. من بين قواعد المزج المقترحة، قواعد Kay كانت هي الافضل في تقيم مشتقات الحرارة.

INTRODUCTION

Thermodynamic and physical properties of hydrocarbon fluids needed for process design and operation in petroleum industries are usually calculated through various thermodynamic models and equations available in process simulators. Generally there are four categories of thermodynamic models, which are: -

- Equations of state model.
- 2- Empirical equations and generalized correlations.
- 3- Activity coefficient models.
- 4- Specific models.

Among many equations of state proposed for predicting phase behavior of hydrocarbon (non-polar) systems, cubic equations of state have been widely used in the reservoir simulation because of their simplicity and accuracy. Soave-Redlich-Kwong (1972) and the Peng-Robinson (1976) cubic equations of state have enjoyed widespread acceptance in the petroleum industries. The purpose of this work is to report the results of simultaneous PVT, thermodynamic properties and vapor-liquid equilibrium prediction for pure hydrocarbons and their mixtures. Also transport properties calculated from empirical functions in temperature and density. The two equations of state mentioned above were used to perform vapor-liquid equilibrium calculation first and then to calculate thermodynamic and transport properties. Also bubble point and dew point pressures and temperatures were predicted using four sets of binary interaction parameter for PR Eos and two sets for SRK Eos. Values of this parameter between C_{7+} and other component have been computationally evaluated and a suggestion to used the last set of PR Eos with SRK Eos.

Thermodynamic properties such as enthalpy, entropy, heat capacity at constant pressure and volume, isothermal and adiabatic Joule-Thomson coefficients, isentropic pressure-temperature coefficient, and adiabatic temperature exponent were calculated analytically from the equations of state. In calculation of heat capacity, four different mixing rules have been proposed to evaluate the temperature derivatives in case of mixtures. Also transport properties such as viscosity, thermal conductivity, and sonic velocity were estimated using different methods and correlations. All calculated properties were compared with corresponding available experimental data.

EQUATIONS OF STATE

The Soave-Redlich-Kwong equation (1972) has the following form:

$$p = \frac{RT}{V_m - b} - \frac{a_T}{V_m(V_m + b)} \tag{1}$$

with; $m = 0.48 + 1.574\omega - 0.176\omega^2$ (2)

$$\alpha = \left(1 + m\left(1 - T_r^{0.5}\right)\right)^2 \tag{3}$$

$$a_T = a_c \,.\, \alpha \tag{4}$$

$$a_c = 0.42747 R^2 T_c^2 / P_c \tag{5}$$

$$b = 0.08664 R T_c / P_c \tag{6}$$

SRK equation of state is a cubic equation in term of compressibility factor Z and this form is the most convenient form used in vapor-liquid equilibrium calculation. This form is:

$$Z^3 - Z^2 + \left(A - B - B^2\right)Z - AB = 0 \tag{7}$$

Where the dimensionless coefficient A and B are defined by the following expressions:

$$A = \frac{a\alpha P}{R^2 T^2} \tag{8}$$

$$B = \frac{bP}{RT} \tag{9}$$

For a mixture, Soave suggested the following mixing rule:

$$a_{T\,m} = \sum_{i=1}^{NC}\sum_{j=1}^{NC}\left[x_i x_j (a_i a_j \alpha_i \alpha_j)^{0.5}(1-k_{ij})\right] \tag{10}$$

$$b_m = \sum_{i=1}^{NC} x_i b_i \tag{11}$$

The term kij is the binary interaction coefficient and it will be discussed in the next section. The fugacity coefficient of component i in a mixture is calculated from the following equation:

$$\ln(\Phi_i) = -\ln(Z-B) + (Z-1)B_i' - (\frac{A}{2^{1.5}B})(A_i' - B_i')\ln\left(\frac{B}{Z}+1\right) \tag{12}$$

Where $B_i' = \frac{b_i}{bm}$ (13)

$$A_j' = \frac{1}{a_{tm}}\left[2a_{Tj}{}^{0.5}\sum y_i a_{Ti}{}^{0.5}(1-K_{ij})\right] \tag{14}$$

Peng-Robinson Eos has the following form:

$$P = \frac{RT}{(V_m - b)} - \frac{a\alpha}{V_m(V_m + b) + b(V_m - b)} \tag{15}$$

where α is calculated from eq. (3). However, the parameter m is calculated according the following equation:

$$m = 0.3746 + 1.5423\omega - 0.2699\omega^2 \tag{16}$$

For PR EOS, the constants **a** and **b** are defined by the following equations:

$$a = 0.45724R^2T_c^2/P_c \tag{17}$$

$$b = 0.0778RT_c/P_c \tag{18}$$

In vapor-liquid calculation for mixture Peng–Robinson suggested the same mixing rule of Soave, i.e. eq. (10) and eq. (11). Compressibility factor are calculated from the following equation by employing Newton–Raphson method:-

$$Z^3 + (B-1)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0 \tag{19}$$

Where A and B are calculated from eq. (8) and eq. (9). The fugacity coefficient of component i in a mixture is calculated from the following equation:

$$\ln(\Phi_i) = -\ln(Z-B) + (Z-1)B_i' - (\frac{A}{2^{1.5}B})(A_i' - B_i')\mathrm{Ln}\left(\frac{Z + 2.414B}{Z - 0.414B}\right) \tag{20}$$

Where $A^{'}$ and $B^{'}$ determine by eq. (13) and eq. (14) respectively.

The main causes which lead to select SRK and PR equations of state to predict the vapor –liquid equilibrium are:

1- Its parameters are known for many pure compounds.
2- Its interaction parameters are available for numerous binary mixtures.
3- Since its constants are fitted to vapor pressure data it is reliable for vapor-liquid equilibrium calculations.

BINARY INTERACTION PARAMETER

Typically all mixing rules used to determine equation of state parameters for multicomponent mixtures are utilized binary interaction parameter. This parameter is usually assumed to be independent of temperature, pressure, and composition. However, some authors introduced values for K_{ij} as a function of temperature.

Generally there are three different categories of binary interaction parameter that have been used by the investigators with Peng-Robinson and Soave-Redlich-Kwong equations of state. These categories are as following:

- In first category all binary interaction parameter values are set to be equal zero depending on the above assumption.
- In the second category K_{ij} for hydrocarbon pairs is taken as zero, while K_{ij} between CO_2, N_2, H_2S and hydrocarbons has been determined experimentally.
- In the third category K_{ij} between hydrocarbons themselves and non-hydrocarbons has been determined experimentally for each equation of state.

In this study, four different sets of binary interaction parameter were used with PR Eos. In the first set, values of binary interaction parameter are taken to be zeros. Table (1) and Table (2) show the values proposed by Brusilovsky and Prausitz (1968) which represented the second and third sets. The last set used with PR Eos is representing by equation proposed by Gao (1992) as a function of critical compressibility factor, which is:

$$(1-K_{ij}^{PR}) = [2(T_{ci}T_{cj})^{1/2} /(T_{ci}+T_{cj})]^{Z_{cij}} \tag{21}$$

$$Z_{cij} = \frac{Z_{ci}+Z_{cj}}{2} \tag{22}$$

Where Z_{ci} is the critical compressibility factor for pure component i and it can be calculated form the following equation:

$$Z_c = \frac{P_c V_c}{RT_c} \tag{23}$$

Where these critical properties are available in the literatures (McCain, 1990) for any component except heptane-plus. Edmister (1984) show a simple relationship of Z_c with acentric factor ω , which obtained directly from the Pitzer-type Z-tables of Lee-Kesler (1975). This relationship illustrated by equation (24).

$$Z_c = 0.2901 - 0.0879\omega \tag{24}$$

By calculation of critical compressibility factor for heptane-plus, and then using eq. (22) and eq. (21), binary interaction parameters between heptane-plus and other components are calculated where this study is the first one that considered this parameter between the plus fraction and other components.

Table (1) *Binary Interaction Parameters for Peng-Robinson equation According to Brusilovsky*

Comp -onent	C_2	C_3	i-C_4	n-C_4	i-C_5	n-C_5	C_6	C_7	C_8	C_9	C_{10}	N_2	CO_2	H_2S
C_1	0.005	0.01	0.035	0.025	0.050	0.030	0.030	0.035	0.040	0.040	0.045	0.025	0.105	0.070
C_2		0.005	0.0	0.010	0.010	0.010	0.020	0.020	0.020	0.020	0.020	0.010	0.130	0.085
C_3			0.0	0/0	0.015	0.002	0.010	0.005	0.005	0.005	0.005	0.090	0.125	0.090
i-C_4				0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.095	0.115	0.075
n-C_4					0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.095	0.115	0.075
i-C_5						0.0	0.0	0.0	0.0	0.0	0.0	0.100	0.115	0.070
n-C_5							0.0	0.0	0.0	0.005	0.0	0.100	0.115	0.070
C_6								0.0	0.0	0.0	0.0	0.110	0.115	0.070
C_7									0.0	0.0	0.0	0.115	0.115	0.060
C_8										0.0	0.0	0.120	0.115	0.060
C_9											0.0	0.120	0.115	0.060
C_{10}												0.125	0.115	0.055
N_2													0.0	0.130
CO_2														0.135

Table (2) *Binary Interaction Parameters for Peng-Robinson equation According to Prausnitz*

Comp -onent	C_2	C_3	i-C_4	n-C_4	i-C_5	n-C_5	C_6	C_7	C_8	C_9	C_{10}	N_2	CO_2	H_2S
C_1	0.0	0.017	0.030	0.027	---	0.027	0.040	0.037	0.052	0.050	0.042	0.031	0.098	---
C_2		0.0	-0.005	0.010	0.009	---	-0.040	0.007	0.018	---	0.014	0.042	---	---
C_3			-0.008	0.003	0.012	0.028	-0.001	0.007	---	---	0.0	0.091	0.124	---
i-C_4				-0.002	----	---	---	---	---	---	---	---	0.131	0.049
n-C_4						0.017	-0.007	0.004	---	---	0.008	0.149	0.135	---
i-C_5														
n-C_5								0.010	---	---	---	---	0.127	---
C_6													0.110	---
C_7														
C_8														
C_9														
C_{10}													0.113	---
N_2													-0.012	0.176
CO_2														0.096

With SRK Eos the first set of binary interaction was also representing by zeros, Table (3) shows the values of this parameter as proposed by Prausitz (1968), which represented the second set. If one examined PR and SRK equations of state he easily can recognize a large similarity between them, for example their parameters a_T and b are function for the same variables, their dimensionless parameters A, B have the same equation, and their parameters are evaluate for the case of a mixture using the same mixing rules. Therefore, we proposed that the same vales of binary interaction parameter could be used for SRK EOS as well as PR Eos. In this study, the Gao equation (1992) (set (4)), which used with PR Eos, has been used with SRK Eos.

Table (3) *Binary Interaction Parameters for SRK Equation of State*

Compound	*H_2S*	*CO_2*	*N_2*
H_2S	---	0.102	0.140
CO_2	0.102	---	-0.022
N_2	0.140	-0.022	---
Methane	0.085	0.0973	0.0319
Ethane	0.0829	0.1346	0.0388
Propane	0.0831	0.1018	0.0807
n-Butane	0.0609	0.1474	0.1007
n-Pentane	0.0697	0.1278	---
Hexane	---	---	0.1444
Heptane	0.0737	0.1136	---
Octane	---	---	---
Nonane	0.0542	---	---
Decane	0.0464	0.1377	0.1293

TYPE OF RESERVOIR FLUIDS

Generally there are five types of reservoir fluids. The types are usually classified by the relationship of the reservoir temperature to the critical temperature and the cricondentherm of the mixtures, and by the surface conditions. The fluid types are; Dry Gas, Wet Gas, Retrograde Gas, Volatile Oil, and Black Oil

In this study, the classification of McGlashan and Peden (1981) for the natural hydrocarbons has been used to determine the type of fluid of interest. The suggested classification is shown in Table (4).

CHARACTERIZATION SCHEME FOR HYDROCARBON SYSTEMS

Vapor-liquid equilibrium and thermodynamic properties calculations generally require critical properties, molecular weight, and acentric factor as input data. Over the years, the critical properties have been measured and compiled for many hydrocarbons and other substances. For methane through decane and the impurities (nitrogen, carbon dioxide, and hydrogen sulfide), the critical pressure, critical temperature, and acentric factor are given in Table (5) (McCain, 1990).

Table (4) *Typical Compositions of Hydrocarbon Fluids*

Type of Fluid	*Methane + Impurities (mol %)*	*Intermediates (mol %)*	*Heptane Plus (mol %)*
Dry Gas	90	9	1
Retrograde Gas	70	22	8
Volatile Oil	55	30	15
Black Oil	30	35	35

Table (5) *The Constant Physical Properties of Pure Hydrocarbon Substances*

Compound	Critical Pressure Psia	Critical Temperature R°	Molecular Weight Ibm/Ib-mole	Acentric Factor *w*
Nitrogen	493.1	227.6	28.0134	0.0372
Carbon dioxide	1071	547.91	44.01	0.2667
Hydrogen sulfide	1300	672.45	34.08	0.0948
Methane	666.4	343.04	16.043	0.0104
Ethane	706.5	549.76	30.07	0.0986
Propane	616	665.68	44.097	0.1524
I-Butane	527.9	734.65	58.123	0.1848
N-Butane	550.6	765.3	58.123	0.1995
I-Pentane	490.4	828.7	72.150	0.2280
N-Pentane	488.6	845.4	72.150	0.2514
Hexane	436.9	913.4	86.177	0.2994
Heptane	396.8	972.4	100.204	0.3494
Octane	360.7	1024.5	114.231	0.3977
Nonane	331.8	1072.6	128.258	0.4445
Decane	305.2	1111.7	142.258	0.4898

As it well known that most laboratory analyses of produced fluids end with some residual or plus fraction. Typically this is C_{7+}. So there is a need to obtain the physical properties of the plus fraction to perform equation of state calculations. In this study, Riazi and Daubert (1980) correlation has been used for estimate the physical properties of plus fraction with Peng-Robinson equation of state. Their equation has the form:

$$\theta = a(T_B)^b \left(\gamma_{c_7^+}\right)^C \qquad (25)$$

Where (θ) is a physical property to be predicted, $\gamma_{c_7^+}$ specific gravity of plus fraction, and (a, b, c) are correlation constants as shown in Table (6).

Mahdi (2002) modification of Riazi and Dubert correlation has been used to predicate the critical properties of the heavy fractions with Soave-Redlich-Kwong equation of state. The equation has the same form of equation (25) but with different values for the constants (a, b, c). The values of these constants are shown in Table (7). With both equations of state, the value of the boiling point has been estimated from Whitson relationship (15) which represented the following equation:-

$$T_B = \left[4.5579 (M_{C_7^+})^{0.15178} \gamma_{c_7^+}^{0.15427} \right]^3 \tag{26}$$

where T_B is the boiling point in degree Rankine. Also the acentric factor has been estimated by Edmister approximation relationship, which has the following form (Mahdi (2002)):

$$\omega = \frac{3}{7}\left[\frac{\log P_C}{T_C / T_B - 1} \right] - 1 \tag{27}$$

where P_c in atmospheres.

Table (6) *Constant for Riazi and Dubert Correlation*

θ	*a*	*b*	*c*
M_w	$4.5673*10^{-5}$	2.1962	-1.0164
T_c	24.2787	0.58848	0.3596
P_c	$3.12281*10^{9}$	-2.3125	2.3201
V_c	$7.5214*10^{-3}$	0.2896	-0.7666

Table (7) *Constants for Mahdi Modification of Riazi and Dubert Correlation*

θ	a	b	c
T_c	24.2787	0.58848	0.3596
P_c	$3.12281*10^{9}$	-2.3125	2.3201

THERMODYNAMIC PROPERTIES FROM CUBIC EQUATION OF STATE

In the classical thermodynamic framework it is possible to obtain typical relationships for the calculation of enthalpy, entropy, fugacity and other thermodynamic properties. These properties can be related to operating variables of the processes, e.g. the temperature of a fluid in a heat exchanger. It is, therefore, important to establish relationships between the properties and independent variables like temperature or pressure. Such relationships for thermodynamic properties of fluids can be obtained using equations of states.

In this section, expressions for enthalpy, entropy, and heat capacity departures of a mixture are derived. The thermodynamic property expressions for a pure substance are not separately derived here, because the mixture expressions also apply to pure substances.

Enthalpy Departure

- For SRK Eos, isothermal enthalpy departure expression is given by:

$$\frac{H-H^*}{RT}=Z-1-\frac{A}{B}\left[1-\frac{T}{a}(\frac{da}{dT})\right]\ln\left(1+\frac{B}{Z}\right) \qquad (28)$$

where:

$$T(\frac{da}{dT})=-\sum_i^N\sum_j^N X_iX_jm_j(a_iac_jT_{ri})^{0.5}(1-k_{ij}) \qquad (29)$$

- For enthalpy departure is given by the following equation:

$$\frac{H-H^*}{RT}=Z-1-\frac{A}{2^{1.5}B}\left[1-\frac{T}{a}(\frac{da}{dT})\right]\ln\left(\frac{Z+(2^{0.5}+1)B}{Z-(2^{0.5}-1)B}\right) \qquad (30)$$

where T(da/dT) is given by eq. (29) too.

Entropy Departure

- For SRK Eos:

$$\frac{S-S^*}{R}+\ln\frac{P}{P^*}=\ln(Z-B)+\frac{A}{B}\left[\frac{T}{a}\frac{da}{dT}\right]\ln\left(1+\frac{B}{Z}\right) \qquad (31)$$

- For PR Eos:

$$\frac{S-S^*}{R}+\ln\frac{P}{P^*}=\ln(Z-B)+\frac{A}{B}\left[\frac{T}{a}\frac{da}{dT}\right]\ln\left(\frac{Z+(2^{0.5}+1)B}{Z-(2^{0.5}-1)B}\right) \qquad (32)$$

Where P^* is equal to 14.7 psia.

HEAT CAPACITY DEPARTURE

The deviation of the isobaric specific heat values from ideal gas state can be expressed on the basis of the definition $C_P = \left(\frac{\partial H}{\partial T}\right)_P$ from classical thermodynamics. One can use eq. (28) to derive the expression of heat capacity departure; however, the above relationship is more convenient and widely used. Also, in all literatures, which have been surveyed in this study, we found only the expression of the isobaric heat capacity departure of a pure component derived from Peng-Robinson equations of state. Therefore, the expressions of isobaric heat capacity for a multicomponent mixture have been derived in this study by both selected equations of state, which are also applied to pure components with restrictions of N =1, and K_{ij} = 0. For SRK Eos we got:

$$C_P-C_P{}^*=R\left[(Z-1)+T(\frac{\partial Z}{\partial T})_P-\frac{1}{Rb}\left(\ln(\beta)(\frac{\gamma}{T}-\eta)+\frac{\theta}{T}(\gamma-a_T)\right)\right] \qquad (33)$$

Where $\beta=1+\frac{B}{Z}$ (34)

$$\gamma=T(\frac{da}{dT})=-\sum_i^N\sum_j^N X_iX_jm_j(a_iac_jT_{ri})^{0.5}(1-k_{ij}) \qquad (35)$$

$$\eta=\frac{\partial}{\partial T}T(\frac{da}{dT})=-0.5\sum_i^N\sum_j^N X_iX_jm_ja_{cj}(a_{Ti}T_{rj})^{-0.5}\left[\frac{a_{Ti}}{T_{cj}}-\frac{a_{ci}\alpha_i{}^{0.5}m_iT_{rj}}{(T_{ci}T)^{0.5}}\right]. \qquad (36)$$

$$\theta=\frac{\partial}{\partial T}\ln(\beta)=\frac{-1}{T}\frac{B}{Z+B}(1+T/Z(\frac{\partial Z}{\partial T})_P) \qquad (37)$$

$$(\frac{\partial Z}{\partial T})_P = \frac{\left[-2B^2 - B + 2A + \frac{AmT_r^{0.5}}{\alpha^{0.5}}\right]Z - 3AB - \frac{ABmT_r}{\alpha^{0.5}}}{T\left[3Z^2 - 2Z - B^2 - B + A\right]} \tag{38}$$

- For Peng-Robinson equation of state

$$C_P - C_P{}^* = R\left[(Z-1) + T(\frac{\partial Z}{\partial T})_P - \frac{1}{2^{1.5}Rb}\left(\ln(\beta)(\frac{\gamma}{T} - \eta) + \frac{\theta}{T}(\gamma - a_T)\right)\right] \tag{39}$$

Where $\beta = \frac{Z + 2.414B}{Z - 0.414B}$ (40)

$$\gamma = T(\frac{da}{dT}) = -\sum_i^N \sum_j^N X_i X_j m_j (a_i ac_j T_{ri})^{0.5}(1 - k_{ij}) \tag{41}$$

$$\eta = \frac{\partial}{\partial T}T(\frac{da}{dT}) = -0.5\sum_i^N \sum_j^N X_i X_j m_j a_{cj}(a_{Ti}T_{rj})^{-0.5}\left[\frac{a_{Ti}}{T_{cj}} - \frac{a_{ci}\alpha_i{}^{0.5} m_i T_{rj}}{(T_{ci}T)^{0.5}}\right] \tag{42}$$

$$\theta = \frac{\partial}{\partial T}\ln(\beta) = \frac{-1}{T}\left[\frac{T(\frac{\partial Z}{\partial T})_P + 0.414B}{Z - 0.414B} - \frac{T(\frac{\partial Z}{\partial T})_P - 2.414B}{Z + 2.414B}\right] \tag{43}$$

$$(\frac{\partial Z}{\partial T})_P = \frac{BZ^2\left[6B^2 + 2B - 2A - \frac{AmT_r^{0.5}}{\alpha^{0.5}}\right]Z + 3B^3 + 2B^2 - 3Ab - \frac{ABmT_r}{\alpha^{0.5}}}{T\left[3Z^2 + 2(B-1)Z - 3B^2 - 2B + A\right]} \tag{44}$$

To applying the above two equations to predict the isobaric heat capacity of a multicomponent mixture, the term $\frac{mT_r^{0.5}}{\alpha^{0.5}}$ of mixture must be evaluated first. None of the surveyed literature illustrated how to evaluate this term even ones predict heat capacity by both equations of state. In this study, the following mixing rules have been proposed to evaluate the required term for a mixture:

1. Use of Kay's additive (5) rules to calculate mixture w_m, Tcm, Pcm, then
   $T_r = T/Tc_m$
   $\alpha_m = \left(1 + m_m\left(1 - T_r^{0.5}\right)\right)^2$
   $m_m = 0.48 + 1.574\omega - 0.176\omega^2$ with SRK Eos and
   $m_m = 0.3746 + 1.5423\omega - 0.2699\omega^2$ with PR Eos.

2. Molal average mixing rule which is given by:

$$\left(\frac{mT_r}{\alpha^{0.5}}\right)_m = \sum_{i=1}^N X_i \frac{m_i T_{ri}}{\alpha_i^{0.5}} \tag{45}$$

3. Van der Waal's mixing rule, which is given by:

$$\left(\frac{mT_r}{\alpha^{0.5}}\right)_m = \sum_{i=1}^{N}\sum_{j=1}^{N} X_i X_j \frac{m_i^{0.5} m_j^{0.5} T_{ri}}{(\alpha_i^{0.5}\alpha_j^{0.5})^{0.5}}(1-k_{ij}) \tag{46}$$

4. Herning and Zipper mixing rule which is given by:

$$\left(\frac{mT_r}{\alpha^{0.5}}\right)_m = \frac{\sum_{i=1}^{N} X_i \frac{m_i T_{ri}}{\alpha_i^{0.5}} M_{wi}}{\sum_{i=1}^{N} X_i M_{wi}} \tag{46}$$

Other Thermodynamic Properties

- Heat capacity at constant volume: From the fundamental property relations, the following relationship between C_V and C_P has been used to calculate the isochoric heat capacity:

$$C_V = C_P - RT\left[\frac{Z}{T} + \left(\frac{\partial Z}{\partial T}\right)_P\right] \tag{47}$$

In this equation universal gas constant R must be in Btu/Ib-mole-R.

- Joule-Thomson effects: where the adiabatic coefficient is given by the following expression:

$$\eta = \frac{RT^2}{C_P P}\left(\frac{\partial Z}{\partial T}\right)_P \tag{48}$$

and the isothermal coefficient is given by:

$$\xi = \left(\frac{\partial T}{\partial P}\right)_S = \frac{RT}{C_P P}\left[Z + T\left(\frac{\partial Z}{\partial T}\right)_P\right] \tag{49}$$

- Sonic velocity:

$$\text{Uf} = [(g_c / Mw)(kRT)(Z + \rho(\partial Z/\partial\rho)_T)]^{1/2} \tag{50}$$

For PR Eos:

$$(\partial Z/\partial\rho)_T = -\frac{(\partial P/\partial\rho)_T (Z^2 B + Z(A-2B-6B^2) + (2B^2+3B^3-2AB))}{P(3Z^2 + Z(2B-2) + (A-2B-3B^3))} \tag{51}$$

For SRK Eos:

$$\left(\frac{\partial Z}{\partial\rho}\right)_T = \frac{-\left(\frac{\partial P}{\partial\rho}\right)_T (ZA - ZB - 2AB - 2ZB^2)}{P(3Z^2 - 2Z - B + A - B^2)} \tag{52}$$

IDEAL GAS STATE THERMAL PROPERTIES

The thermodynamic property calculation methods presented in the previous sections are for calculating the isothermal departure function of the properties from their ideal gas state values for pure fluids or mixtures. Therefore, it is imperative to know the ideal gas state properties for the calculation of the absolute values of thermodynamic properties of real fluids at a given temperature and pressure.

For pure components and defined composition mixture we utilize the Aly and Lee (1981) equations for calculating ideal gas state thermal properties. For all pure components except hydrogen sulfide, the following equations have been used:

$$C_P{}^* = B + C\left[\frac{(D/T)}{\sinh(d/T)}\right]^2 + E\left[\frac{(F/T)}{\cosh(F/T)}\right] \tag{53}$$

$$H^* = BT + CT(\frac{D}{T})\coth(\frac{D}{T}) - ET(\frac{F}{T})\tanh(\frac{F}{T}) + A \tag{54}$$

$$S^* = B\ln T + C\left[\frac{D}{T}\coth(\frac{D}{T}) - \ln\sinh(\frac{D}{T})\right] - E\left[\frac{F}{T}\tanh(\frac{F}{T}) - \ln\cosh(\frac{F}{T})\right] + G \tag{55}$$

Where temperature in ^oK, enthalpy in Cal/gm-mole, heat capacity and entropy in Cal/gm-mole ^oK. One of the prominent features of the above equations is that the parameters (A, B, C, D, E, F, and G) have physical meaning through their statistical mechanics derivation. For example, the constant B represents the contributions due to the translational and rotational motions of the molecules, and constant D characterizes vibrational temperature of the polyatomic molecules.

For hydrogen sulfide, the correlation of Passut and Danner (1972) has been used. This correlation represented by Eqs, 2.28, 2.29, and 2.30. Values of the equations constant are:
A = -0.61782, B = 0.238575, C = -0.024457 E-3, D = 0.044067 E-6, E = -0.130126 E-10, F = 0.144852 E-14, and G = -0.045932.

For undefined mixtures and petroleum fractions a method named “Equivalent Pure Component” has been used. This method is simple and generally involving only one parameter. It states that if there is an undefined substance (pure or mixture) has a value for certain variable equal to that of a pure component, then they will have the same properties (Sehgal, 1968). Since that the ideal gas thermal properties are a function of the molecular weight, so this variable can be adapted as correlated parameter. This method has two disadvantages, the first one that it restricted to mixtures of homogenous series. The second one is that for large molecular weight mixtures, ideal gas thermal properties must be available for heavy hydrocarbon components. In this study, this method restricted to molecular weight of 282 (of Eicosane) Ibm/Ib-mole.

RESULTS AND DISCUSSION

The objective of current study was to develop a complete package for calculating of physical and thermodynamic properties mainly for hydrocarbon and petroleum fluids by means of two equations of state in vapor and liquid phases. Peng-Robinson and Soave-Redlich-Kwong equations of state have been used for volatile and black oils respectively in this package, these equations used to perform the following calculation types: -

- Fluid properties prediction (P & T specified).
- Bubble point pressure calculation (T specified).
- Bubble point temperature calculation (P specified).
- Dew point pressure calculation (T specified).
- Dew point temperature calculation (P specified).
- Gas-oil separation calculations (isothermally and adiabatically).

In these calculation types the following properties are calculated:-

- Phase region and Phase envelope.
- Vapor and liquid mole fractions (V, L).
- Phase’s compositions (y_i, x_i).
- Equilibrium ratios (K-values).
- Compressibility factor (Z).
- Density.
- Enthalpy (H).
- Entropy (S).
- Isobaric heat capacity (Cp).

- Isochoric heat capacity (Cv).
- Isothermal and adiabatic Joule – Thomson coefficients.
- Adiabatic temperature exponent.
- Surface tension.
- Viscosity.
- Thermal conductivity.
- Speed of sound.

Many correlations for viscosity, thermal conductivity, surface tension and sixty tables compare the computed values of phase region, vapor mole fraction, vapor and liquid phases compositions, bubble point pressure and temperature, enthalpy, entropy, heat capacity, adiabatic and isothermal Joule-Thomson coefficients and sonic velocity for pure component, binary mixtures, multicomponent mixtures, volatile and black oils samples (The mole composition and properties of plus fraction of hydrocarbon mixtures and oil samples are tabulated in Appendix A) in different phase regions not included in these few papers because little space available. So only the most important results and their discussions presented in this section

The validity of both equations of state is examined by using absolute relative deviation (RD) and absolute average percentage error (AAPE) according to the following equations:-

$$RD = Abs(\frac{Exp - Cal}{Exp}) \times 100.0 \tag{56}$$

$$AAPE = \frac{\sum RD}{N} \tag{57}$$

In addition to the comparisons with the corresponding available experimental data, the calculated properties from the present package are compared with those calculated by other internationally developed software, namely PhysPros and MixProps. A trial version for 14 days for these two software were gotten from G&P Engineering Software company (http://www.gpengineeringsoft.com) that specializes in delivering high quality chemical engineering software for chemical professionals. PhysPors is used for application of pure component, thermophysical property database and property estimating. MixProps is used to calculate a two-phase vapor-liquid equilibrium, thermodynamic, and transport property for technical professionals using five equations of state including SRK and PR.

Phase Region

In order to check the capability of equations of state to predict the phase region of a mixture, experimental data of simple hydrocarbon mixtures (binaries) have been used. Table (9) shows the experimental and predicted phase regions for Ethane-n-Butane mixtures (Wolfe, 1966) using PR and SRK Eos at 400 Psia pressure and temperature range from 50 to 250 ° F. This table illustrates the effect of the binary interaction parameter on estimation of phase region.

Regardless of the value of binary interaction parameter, PR Eos predicts the phase region with reasonable accuracy as shown in Table (9). It is clear that the 4th set of K_{ij} and MixProps software give the exact results, also 1st set give good agreement with experimental phase regions. While 2nd and 3rd sets give results with lower accuracy especially for mixtures B2, and B3. For SRK Eos both sets give good results and no improvement noted for one over another one. SRK results are better matched with experimental results than those obtained by MixProps software. The second set is eliminated from this comparison because it considers the values of binary interaction parameter only between non-hydrocarbon and hydrocarbon components and since the investigated binaries do not contain non-hydrocarbon component, it will make no difference in results from those of the first set.

Table 9 - *Comparison of Predicted and Experimental Phase Region for Ethane-n-Butane Mixtures At 400 psia*

Sample No	Temp. (°F)	Exp.	PR					SRK		
			Cal (1)	**Cal (2)**	**Cal (3)**	**Cal (4)**	**MixProps**	**Cal (1)**	**Cal (3)**	**MixProps**
B1	246.2	V	V	V	V	V	V	V	V	V
B2	205.4	V	V	V	V	V	V	V	V	V
B3	166.0	V	V	V	V	V	V	V	V	V+L
B4	124.8	V	V	V	V	V	V	V	V	V
B5	75.0	V	V+L	V	V	V	V	V+L	V	V
B1	209.1	L	L	L	L	L	L	L	L	L
B2	129.0	L	L	V+L	V+L	L	L	L	L	L
B3	88.4	L	L	V+L	V+L	L	L	L	L	V+L
B4	63.8	L	L	L	L	L	L	L	V+L	V
B5	47.8	L	L	L	L	L	L	L	L	V

V = Vapor, L = Liquid

Bubble Point Pressure Prediction

Bubble point pressures of different hydrocarbon mixtures have been calculated by PR Eos with its four sets of binary interaction parameter and compared with experimental pressures and those calculated by MixProps software (Table (10). It is obvious that PR Eos gives very good agreements with experimental data for these mixtures, which included binary, ternary, and multi component mixtures. The capability of the fourth set of K_{ij} to improve the results appear again specially over the first set, however, all sets gave results much more accurate than those calculated by MixProps software which gave AAPE of 14.37 while first set in the present program gave 5.031 (maximum). Also bubble point pressure has been calculated by SRK Eos with its three sets for binary interaction parameter for these hydrocarbon mixtures and presented in the same table. SRK Eos gives very good agreements with experimental data and the second set of K_{ij} gave the minimum error of 2.85 %, and all sets gave results much more accurate than those of MixProps software.

With respect to petroleum fluids, bubble point pressure has been calculated for five volatile oil samples and presented in Table (11). In general, agreement between predicted and experimental results is good. However, in some instances, significant disagreement was noted. While it is not possible to explain such disagreement with certainty, close scrutiny of the experimental data suggests that for some of the reported points there may be appreciable experimental error specially when these experimental data taken from one reference as the case of volatile oils.

Many studies have been used bubble point pressure as the **basis** to conclude that PR Eos is more suitable for predicting of volatile oils phase behavior. Most of these studies predicted Pb by PR and SRK Eos with zero binary interaction parameter, and found the PR give less AAPE for volatile systems than black ones.

Table (12) shows the predicted results of Pb for ten black oil samples by PR Eos. As in the other studies, PR Eos gives AAPE for black oils great than that of volatile oils with zero binary interaction parameter, also this is the case of the 2nd and 3rd sets of K_{ij}, but PR Eos give **very good** agreement with

Table (10) – *Comparison of Experimental and Calculated Bubble Point Pressure by PR and SRK Eos for Binary, Ternary and Multicomponent Mixtures*

Sample No	*Temp °F*	*Bubble Point Pressure (Psia)*									
		Exp.	**SRK**				**PR**				
			Cal (1)	**Cal (2)**	**Cal (3)**	**MixProps**	**Cal (1)**	**Cal (2)**	**Cal (3)**	**Cal (4)**	**MixProps**
B7	-130	483.56	488.261	488.261	488.373	488.732	485.649	485.73	485.806	485.787	486.079
T1	-179.8	488.5	444.973	489.225	450.410	447.5	441.42	548.5	472.32	447.27	447.5
T2	-50	400	396.364	396.364	408.183	341.974	388.751	395.283	395.669	401.179	335.631
M1	-144	100	109.366	112.704	121.097	113.938	104.575	114.596	119.639	115.845	108.782
M1	-100	200	196.876	200.165	213.674	183.378	188.683	202.408	209.930	205.443	176.095
M1	-81	250	240.969	244.141	259.618	221.778	231.604	246.705	255.197	250.543	213.646
M1	-62	300	287.9012	290.922	308.074	261.628	277.754	293.913	303.204	298.376	252.926
M1	-24	400	388.141	390.785	410.215	344.149	377.614	395.067	405.544	400.575	335.319
M1	12	500	488.759	490.998	511.152	423.057	479.347	497.019	507.809	503.065	415.368
M1	47	600	590.493	592.329	611.863	498.134	583.348	600.219	610.663	606.369	492.51
M1	76	700	676.84	678.347	696.464	557.38	672.094	687.641	697.380	693.441	553.872
M1	102	800	754.448	755.668	771.843	762.548	752.025	765.84	774.551	771.114	603.359
AAPE			**3.76**	**2.85**	**4.675**	**11.8**	**5.03**	**3.41**	**3.4**	**2.9**	**14.37**

B=Binary, T=ternary and M=Multicomponent

Table (11) – *Comparison of Experimental and Calculated Bubble Point Pressure by SRK and PR Eos for Volatile Oil Samples*

Sample No	*Temperature °F*	*Bubble Point Pressure (Psia)*							
		Exp(6)	**PR**			**SRK**			
			Cal (1)	**Cal (2)**	**Cal (3)**	**Cal (1)**	**Cal(2)**	**Cal(3)**	**Cal(4)**
1	210	4452	4082.365	4135.293	4598.849	3958.64	4018.98	3977.95	4484.99
2	264	4900	3731.529	3735.498	4161.018	3643.717	3667.426	3660.7	4092.07
3	210	4300	3587.515	3589.398	3995.562	3505.4	3532.3	3525.31	3929.77
4	210	3982	3934.522	3978.944	4465.389	3828.87	3878.909	3843.83	4374.66
5	12	3556	3835.185	3873.514	4401.388	3739.002	3782.36	3751.32	4323.84
AAPE			**11.55**	**11.28**	**12.27**	**12.83**	**12.33**	**12..58**	**11.45**

experimental pressures for black oils using the fourth set and these results give AAPE (6.55), which is less than that of volatile oils (11.45) themselves. This behavior may be explained as a result for using the fourth set which is the single set that considered binary interaction parameter between C_{7+} and the other components and since black oils contain large amounts of C_{7+}, this will have large effect on any equation involved binary interaction parameter. From the above discussion, one can **conclude** that the selection of the suitable Eos for certain fluids should not be based only on one property, and PR Eos predicts bubble point pressure of black oils with very good accuracies.

Also Table (12) shows the calculated bubble point pressures for these ten black oil samples using SRK Eos which with Gao equation (set (3)) for binary interaction parameter gives very **good** agreement with the experimental data as with PR Eos. First and second sets give results for Pb deviated substantially from experimental data where AAPE was 17.3 and 17.2 respectively as shown in Table (12), but these two sets give errors less than those of PR Eos with first three sets of K_{ij}.

From these entire comparisons one can **note** that for binary, ternary, and multicomponent mixtures PR Eos with Gao equation and SRK with second set approximately gave the same AAPE, which was 2.905 and 2.85 respectively. This point is also true for volatile oil samples (AAPE of 11.45 and 11.28). For black both equations of state with Gao equation also approximately gave the same error of 6.627 and 6.445 respectively. Therefore, a **conclusion** can be made which state that any equation of state utilizing in this study can be used for calculation of Pb for any hydrocarbon mixture (binary, ternary, multicomponent, volatile oil, and black oil) by considering the recommended binary interaction parameter sets. Table (13) shows the recommended binary interaction parameter set for each Eos.

Table (12) – *Comparison of Experimental and Calculated Bubble Point Pressure by PR and SRK Eos for Black Oil Samples*

Sample No	***Temp °F***	***Bubble Point Pressure (Psia)***							
		Exp	**PR**				**SRK**		
			Cal (1)	**Cal (2)**	**Cal (3)**	**Cal (4)**	**Cal (1)**	**Cal (2)**	**Cal (3)**
1	200	2890	2281.78	2339.95	2290.67	2857	2372.43	2372.43	2867.19
2	234	2623	1982.64	1987.41	1985.98	2370.13	2012.513	2011.907	2374.352
3	232	1970	1639.58	1643.88	1642.52	1926.01	1657.502	1657.797	1947.195
4	210	2010	1522.464	1528.889	1527.392	1781.386	1543.564	1543.679	1784.026
5	210	2800	2177.226	2188.741	2185.468	2549.884	2208.326	2208.409	2531.288
6	210	2340	1854.604	1862.647	1860.652	2171.845	1878.55	1878.643	2174.239
7	140	2247	1962.11	1977.51	1973.37	2432.11	2000.919	1991.83	2445.491
7	176	2403	2175.52	2188.56	2185.04	2627	2190.789	2210.352	2619.088
7	210	2643	2353.942	2364.788	2361.789	2797.797	2385.264	2384.676	2799.373
8	220	2620	2163.550	2180.62	2177.052	2495.311	2185.974	2186.631	2491.662
9	205	2420	1700.16	1708.69	1706.54	1995.07	1724.013	1724.237	1998.347
10	210	2375	1999.502	2011.625	2008.47	2312.75	1717.198	1720.13	2033.629
10	176	2218	1855.01	1868.71	1865.17	2181.33	1887.346	1889.512	2192.608
10	140	2062	1680.21	1695.51	1691.61	2015.46	2027.491	2029.087	2318.432
AAPE			**18.601**	**18.030**	**18.262**	**6.627**	**17.307**	**17.254**	**6.445**

Table (13) – *Recommended Sets of K_{ij} for Calculation of Bubble Point Pressure By PR and SRK Eos.*

Sample Type	***PR***	***SRK***
Binary, Ternary, and Multicomponent	Set (4)	Set (2)
Volatile Oil	Set (4)	Set (2)
Black Oil	Set (4)	Set (4)

CONCLUSIONS

Four sets of binary interaction parameter have been used with PR Eos and two with SRK Eos in this study, which indicated that the value of the binary interaction parameter has obvious effect on predicting of different properties especially P-V-T properties of the hydrocarbon mixtures. Also we proposed that the last set of binary interaction parameter, which represented by Gao equation, might be used with SRK Eos as a third set.

Peng- Robinson equation of state with the last three sets of the binary interaction parameter and Soave-Redlich-Kwong equation of state with the last set predict accurately different properties of interested fluids and the last set (Gao equation) for both equations is the better one and it give the minimum errors for large number of the calculated properties.

Using the fourth set of binary interaction parameter, Peng-Robinson equation of state predict bubble point pressure of black oils with very good accuracy, so it can be used with this type of reservoir fluids. Therefore, the selection of suitable equation of state for certain fluids should be not based only on one property. For certain hydrocarbon mixtures (may be binary, ternary, multicomponent, volatile oil, and black oil) both equations of state predict bubble point pressure approximately with the same accuracies using the recommended values for binary interaction parameter, so there are no limitations in use this equation only for certain fluids and other one for other fluids.

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Nomenclature

List of Symbols:

AAPE	Average absolute percentage error.
a, b	Equation of state constants.
C_p	Isobaric heat capacity Btu/Ib-mole. R°.
C_v	Isochoric heat capacity Btu/Ib-mole. R°.
Eos	Equation of state.
K	Equilibrium ratio.
K_{ij}	Binary interaction parameter.
m	Parameter in Eos .
M_w	Molecular weight Ib/Ib-mole.
N	Number of data points.
Nc	Number of components in the mixture.
P	Pressure, Psia
P_b	Bubble point pressure Psia.
P_d	Dew point pressure Psia.
P_r	Reduced pressure.
R	Universal gas constant 10.732 Psia.ft^3/Ib-mole. ° R.
Rd	Relative deviation.
S	Entropy Btu/Ib-mole R°.
Sp.gr	Specific gravity.
T	Temperature F°
T_B	Boiling point temperature, ° R.
ν	Vapor mole per 1 mole of feed.
V_m	Molar volume ft^3/Ib-mole.
Uf	Sonic velocity, ft/sec.
X	Liquid mole fraction.
Y	Vapor mole fraction.
Z	Compressibility factor.
Z_i	Mole fraction of component i in the feed.

Greek Letters:

ω	Acentric Factor
γ_g	Gas specific gravity, (air = 1.0)
Φ	Fugacity coefficient.
ρ	Density of the Fluids, Ibm/ft^3.
η	Adiabatic Joule-Thomson Coefficient, ° R/psia.
ξ	Isothermal Joule-Thomson Coefficient, ° R/psia.

Superscripts:

L	Liquid
V	Vapor
*	Ideal gas state property.

Subscripts:

c Critical Property.

r Reduced property.

APPENDIX (A): Hydrocarbon Samples Compositions

Table A.1- *Mole Compositions of Hydrocarbon Samples Binary, Ternary, and Multicomponent Mixtures Volatile Oils*

Sample No	B1	B2	B3	B4	B5	B7	T1	T2	M1	V1	V2	V3	V4	V5
Mole Percent														
N_2	-	-	-	-	-	-	26.347	-	0.20	0.122	0.135	0.2	-	0.149
$C0o_2$	-	-	-	-	-	-	-	-	0.05	2.955	2.991	0.45	1.6	3.092
H_2S	-	-	-	-	-	-	-	-	-	9.872	9.799	0.08	0.15	9.88
C_1	-	-	-	-	-	94.8	71.358	27.70	23.16	55.236	58.28	55.48	54.87	60.75
C_2	17.49	45.10	65.77	82.18	94.72	-	2.295	52.30	0.050	5.989	6.005	11.83	10.18	6.167
C_3	-	-	-	-	-	5.02	-	20.00	76.53	2.139	2.091	5.77	5.23	2.201
$i\text{-}C_4$	-	-	-	-	-	-	-	-	-	0.248	0.235	0.88	1.08	0.273
$n\text{-}C_4$	82.51	54.90	34.23	17.82	5.28	-	-	-	0.110	0.673	0.688	3.65	3.06	0.744
$i\text{-}C_5$	-	-	-	-	-	-	-	-		0.198	0.205	1.2	1.22	0.23
$n\text{-}C_5$	-	-	-	-	-	-	-	-	-	0.237	0.25	138	1.42	0.283
C_6	-	-	-	-	-	-	-	-	-	0.216	0.245	-	-	0.316
C_7	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C_8	-	-	-	-	-	-	-	-	-	-	-	-	-	-
C_9	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Plus Fraction	-	-	-	-	-	-	-	-	-	22.12	19.06	18.88	21.03	15.92
Total	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Sp.gr of C_n	-	-	-	-	-	-	-	-	-	0.8404	0.824	0.828	0.84	0.822
Mw of C_n	-	-	-	-	-	-	-	-	-	158	154	156	163	150

Table A.2- *Mole Compositions and Properties of Plus Fraction of Black Oils Samples*

Sample No	1	2	3	4	5	6	7	8	9	10	11
Components	Mole Percent										
N_2	-	0.47	0.01	0.70	1.32	1.22	1.66	0.91	0.67	1.66	1.31
Co_2	-	0.35	0.79	0.39	0.42	0.71	1.29	0.16	0.44	1.29	1.31
H_2S	-	-	0.43	-	-	-	-	-	-	-	-
C_1	42.41	29.99	25.89	25.61	34.64	30.55	36.53	36.47	28.77	36.53	31.62
C_2	5.33	11.44	11.49	8.95	10.46	8.86	10.49	9.67	9.22	10.49	9.52
C_3	4.67	6.36	6.98	7.65	6.16	7.22	7.15	6.95	7.47	7.15	7.76
$i\text{-}C_4$	1.55	1.12	1.53	1.49	1.81	1.33	0.94	1.44	1.68	0.94	1.54
$n\text{-}C_4$	2.02	4.07	4.07	4.48	4.56	4.22	5.36	3.93	4.36	5.36	2.74
$i\text{-}C_5$	0.92	1.70	2.08	1.53	1.60	1.39	1.63	1.44	1.68	1.63	1.33
$n\text{-}C_5$	0.86	1.93	2.55	2.42	1.83	2.30	2.26	1.41	2.59	2.26	2.79
C_6	3.13	-	-	-	-	-	-	4.33	-	-	-
C_7	-	-	-	-	-	-	-	-	-	-	-
C_8	-	-	-	-	-	-	-	-	-	-	-
C_9	-	-	-	-	-	-	-	-	-	-	-
Plus Fraction	39.11	42.60	44.03	46.78	37.54	42.20	32.69	33.29	43.10	32.69	40.07
Total	100	100	100	100	100	100	100	100	100	100	100
Sp.gr of C_n	0.895	0.9314	0.9304	0.8947	0.8730	0.8769	0.8739	0.8515	0.8890	0.8739	0.8655
Mw of C_n	267	266.2	286.16	227.64	210	225.4	250	218	222.48	250	191