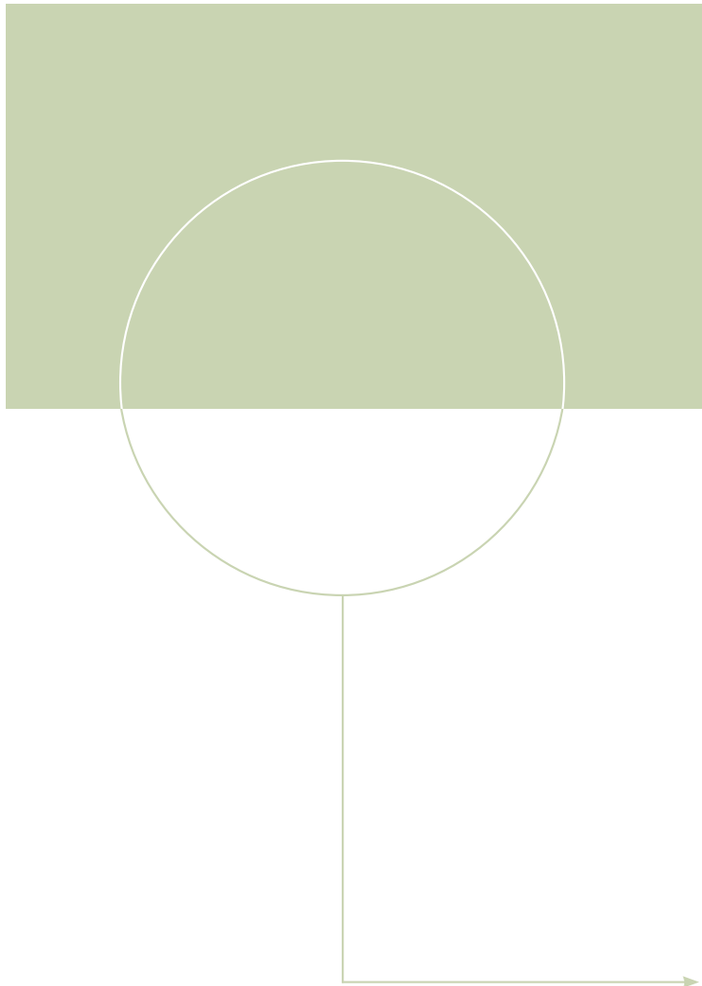

Master's thesis

2019

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Abstract

This thesis develops a new methodology of estimating the amount of PNA compounds in each fraction using laboratory conventional PVT report i.e. using molecular weights and liquid molar volumes (densities and molecular weights) as inputs.

The proposed characterization method use the molecular weights and liquid molar volumes of the heaviest aromatic compounds found in the literature while keeping the classic definitions of the Paraffinic and Naphthenic compounds as in API, Bergman and Robinson-Peng characterization methods. New correlations for the molecular weight,molar volume, critical pressure, critical temperature, acentric factor and boiling points were developed for the new identified aromatics as a function of single carbon number. For the naphthenic and paraffinic compounds, Robinson-Peng correlations are still used.

The new characterization method significantly improves the density conservation compared to Bergman or Robinson-Peng characterization methods. It also conserve the normal to normal paraffin definition (SCN) and ideal liquid molar volume mixing better compared to previous characterizations methods.

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Chapter 1

Introduction

If you wish to converse with me, define your terms – Voltaire

Forged in the above quote is the wisdom that can be applied in the philosophy, debate and argumentation. How many times that people argue while basically agreeing; or agree on a term while meaning totally different things, even the opposite things, while unaware. The very same phenomenon might happen even in the realm of science and engineering.

In petroleum industry, fluids produced vary from region to region, reservoir to reservoir, well to well, or even from the same well as a function of time. Huge sums of money and time are spent to know the chemical make ups and the physical properties of the reservoir and produced fluids. These results from the lab reports are then used in the modelling and tuning of an Equation of State (EOS) or could be used in the reservoir simulation studies (which might require EOS or its predictions).

To make an accurate EOS, it is important to accurately describe the compositions and the amount of each "cut". The better the description of the components making up the petroleum fluid, the better the predictions.[1,2] The trickiest components to describe are those that boil after normal hexane; they are traditionally known as the heptanes-plus (C7+) components. This problem becomes more complicated when the reservoir fluid contain oil because large portion of oils consist of heptanes-plus fractions.

Conventional laboratory compositional tests will provide the components and their relative composition (weight or molar or both). Currently, the laboratories will provide composition up to 36+. However, sometimes the laboratories will not give the molecular weights and the densities of the fractions; while sometimes they will give them, but indirectly. Several efforts have been made to better describe the compositions, molecular weights, specific gravity, critical properties, acentric factors and binary interactions parameters of these cuts. The results are improved quality of EOS models and their predictions.

However, since no two reservoir fluids are exactly alike, treatment of the heptanes-plus

fractions as alike may introduce inaccuracies. For example, for the same boiling point cuts, the chemical make-ups may vary significantly from one fluid to another. In the same way that some fluids may be paraffinic in nature while others being aromatic, the constituent components (cuts) of these fluids can also vary from being too paraffinic or too aromatic. In general, the distribution of the hydrocarbon families as the function of the boiling points are as shown in the Figure 1.1:

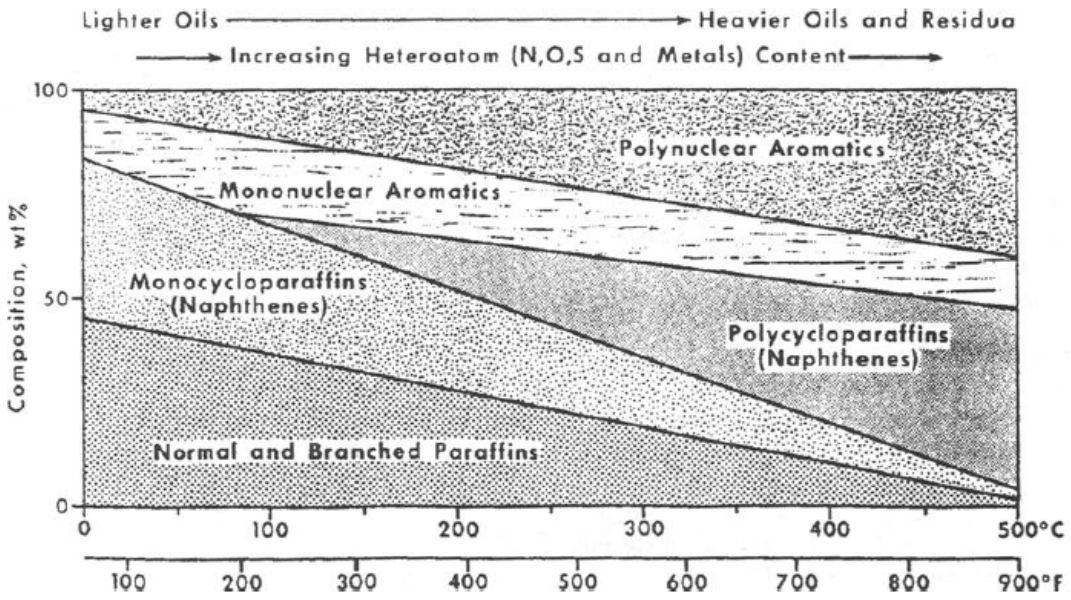

Figure 1.1: Distribution of hydrocarbons families according to normal boiling point[3]

Several authors have tried to establish the parafinicity or aromaticity of different petroleum samples. Others have tried to break down the components in their hydrocarbon groups so as to get better descriptions of the components. Several schemes are in existence: Paraffinic-Aromatic (PA) analysis, Saturates-Aromatic-Resins-Asphaltenes (SARA) analysis and Paraffin-Naphthenic-Aromatic (PNA) analysis, the latter being the most important and widely used in Petroleum Industry.

While several authors have tried to establish the composition of the components through PNA analysis, the methods available cannot be used all the time due to the absence of data that these methods employ, "incomplete" methodology or simply the method do not give reliable results. This thesis is geared into establishing a modified methodology to characterize and establish the compositions of the petroleum fractions. This thesis work has been divided in different chapters: Chapter 2 is a Literature Review that covers aromaticity indicators, EOS parameters and PNA characterization methods; Chapter 3 discusses the challenges and solutions of the existing characterizations; Chapter 4 develops correlations for the new characterization method while Chapter 5 details a step by step application of the new characterization method.

Unless otherwise stated, symbols in the equations have been consistently used. If the same symbol is used to describe multiple quantities, cares have been taken to explicitly describe the situation.

Important Definitions

The following definitions have been adhered to in this work unless stated otherwise.

PNA: Paraffinic, naphthenic and aromatics

SCN: hydrocarbons entailed in the normal to normal paraffins boiling boints. The symbol used in this work is n (not to be confused with the refractive index, which also use n).

Paraffins: normal (unbranched) alkanes. Quantities related are subscripted with p.

Naphthenes: normal-alkyl-cyclohexanes. Quantities related are subscripted with n.

Aromatics: normal-alkyl-cyclobenzene. Quantities related are subscripted with a.

Boiling point: it's a normal boiling point i.e. boiling point at 1 atmospheric pressure. The symbol used in this work is T_b. Unless otherwise mentioned, the temperatures are given in Kelvin throughout this work.

Other quantities will be introduced as they appear in the work.

Chapter 2

Literature Review

Different and sometimes complimenting attempts have been made by different authors to capture the complexity of characterizing heptane-plus (C7+) components. Several have made attempts to describe the molecular weights of the single carbon numbers (SCN). SCN of a particular carbon number, n is defined as the all molecules that have the normal boiling points between normal alkane of n-carbon number and the normal alkane of the previous normal alkane. Some of these characterization include critical properties estimations while some do not. The following are example of the C7+ characterizations:

2.1 Katz-Firoozabadi Characterization

Arguably the most famous of the C7+ is the Katz-Firoozabadi (KF) characterization. They extended the Bergman C7+ characterization from SCN 15 to SCN 45 using Bergman data and their new data.[4] KF characterization contain Molecular weights, boiling points and specific gravity of the fractions. Whitson and Brule calculated critical temperatures, critical pressures and acentric factors using Lee-Keslers correlations for each entry of the SCN component. They also calculated critical volumes using Riazi (Versatile) correlation.[5] The complete characterization is attached in Appendix A.

2.2 Molar Distribution

While KF gives properties of the C7+ fractions, it does not give information on the molar compositions of these fractions. Several models have been proposed that relate the molar compositions to the molecular weights on the components. Because the work of this thesis isn't focusing on the distributions of the components (despite its undeniable importance), an interested reader is advised to look at these models: Exponential model,[6] Gamma model[2] and Riazi model.[7]

2.3 Aromaticity Indicators

There are several measures of the aromaticity factor of the components or the whole fluid based on other secondary properties. However, most of these factors are qualitative in nature and only gives the relative measures. Most of the C7+ characterizations methods discussed later are based on one or several of these factors.

2.3.1 Watson or Universal oil products (UOP) Characterization Factor

The most important characterization factor in petroleum industry for the measure of the aromaticity is, arguably, the Watson Characterization factor (Kw). The Watson characterization factor is defined as:

$$K_w = T_b^{1/3}/\gamma \tag{2.1}$$

where: T_b = normal boiling point in ^{o}R and γ = specific gravity

Kw varies from 11.0 to 12.5 for the paraffinic compounds; 11.0 to 12.5 for the naphthenic compounds and 8.5 to 11.0 for the aromatic compounds.[5] Some literature provides relatively different scale for the three groups with Parafinnic being between 13.2 to 13.6,[3] or 12.5 to 13.5;[8] naphthenic compounds between 10.5 and 13.3 and Aromatic given between 9.5 to 12.5.[3]

2.3.2 Jacoby Aromaticity Factor

Although Jacoby aromaticity factor (Ja) and Kw relationships of molecular weights and densities are similar, the former gives more physically consistent behavior when used to calculate densities of the fractions . Ja is defined as:

$$Ja = \frac{\gamma - 0.8468 + (15.8/M)}{0.2456 - (1.77/M)} \tag{2.2}$$

where: M = Molecular weight

Equation 2.2 above ensures the specific gravities of the fraction increase quickly at lower molecular weights while flattens more at higher molecular weights. Traditionally, Ja ranges between 0 and 1.[5] The higher the number, the more aromatic the sample.

2.3.3 Yarborough Aromaticity Factor

Yarborough (Ya) modified Ja by improving the characterization of the fractions up to C13 and by improving the characterization of the naphthenic content of heavier fractions. The original curves of Yarborough were fit by Equation 2.3.

$$\gamma_i = exp[A_0 + A_2 i + A_3 ln(i)] \tag{2.3}$$

The constants A0 to A3 for different Ya are as shown in Appendix B.1. The Ya ranges between 0 to 80 with higher numbers representing higher aromaticity.[5]

2.3.4 Søreide Factor

Søreide developed correlation between the specific gravity of the fractions and their molecular weights using the Søreide Constant (C_f). The correlation is as shown by Equation 2.4:

$$\gamma_i = 0.2855 + C_f(M_i - 66)^{0.13} \tag{2.4}$$

C_f normally ranges between 0.27 to 0.31 with higher numbers representing higher aromaticity.[5]

2.3.5 Viscosity Gravity Constant

Hill and Coats[3] used viscosity gravity constant (VGC) to determine the molecular type of the sample. VGC can defined by Equations 2.5 and 2.6 depending on the viscosity available.

$$VGC = \frac{10\gamma - 1.0752log(V_{38} - 38)}{10 - log(V_{38} - 38)} \tag{2.5}$$

$$VGC = \frac{\gamma - 0.24 - 0.022log(V_{99} - 35.5)}{0.75} \tag{2.6}$$

where: V_{38} = Viscosity at 38^0C (100^0F) in SUS (Saybolt Universal Seconds) and V_{99} = Viscosity at 99^0C (210^0F) in SUS

Equations 2.5 and 2.6 limit the use of VGC for heavier fractions with kinematic viscosity of approximately 3.8cSt at 100^0F. American Society for Testing and Materials (ASTM) has produced a monograph with wider applications of viscosities at 100^0F that use

specific gravity and kinematic viscosity as inputs to obtain VGC; the monograph is as seen in Appendix C.1.

The typical values for the Paraffinic, naphthenic and aromatic groups are 0.74-0.75, 0.89-0.94 and 0.95-1.13 respectively.[3]

2.3.6 Refractive Intercept

Kurtz and Ward (1935)[3] have used the fact that the refractive index and specific gravity varies linearly within the same hydrocarbon family. The Refractive Intercept (Ri) was then empirically defined as shown in the Equation 2.7 Below

$$R_i = n - \frac{d}{2} \tag{2.7}$$

where: n = refractive index and d = density at 20^0C

The Refractive Intercepts for the Parrafinic, naphthenic and aromatic groups are 1.048-1.05, 1.03-1.046 and 1.07-1.105.[3]

2.3.7 m Factor

A similar approach to refractive intercept has been used by defining a parameter m which is function of refractive index and molecular weight. Since the values of n and 1/M varies linearly within each hydrocarbon family, m was defined as shown in Equation 2.8 below:

$$m = M(n - 1.475) \tag{2.8}$$

The values for m are approximately -8 for paraffinic, -4 to -5 for naphthenic and 2 for aromatic samples.[3]

2.3.8 Huang Factor

Huang (1977) used the fact that paraffinic oils have lower refractive index compared to aromatics to describe aromaticity of the fluids. Huang factor is defined as

$$I = \frac{n^2 - 1}{n^2 + 1} \tag{2.9}$$

Huang factor gives values of 0.26-0.273, 0.278-0.308 and 0.298-0.362 for the paraffinic, naphthenic and aromatic samples respectively.[3]

2.3.9 CH Ratio

The ratio of carbon to hydrogen (CH) is one of the parameter that can be used to distinguish between the three hydrocarbon groups. With normal paraffin fully saturated, the carbon to hydrogen ratio is lower while being higher in aromatics. The CH ration can be calculated using boiling point and specific gravity as shown by Equation 2.10 below:

$$CH = 8.7743X10^{-10}[exp(7.176X10^{-3}T_b + 30.06242\gamma - 7.35X10^{-3}T_b\gamma]T_b^{-0.98445}\gamma^{-18.2753} \tag{2.10}$$

2.3.10 Correlation Index

The US Bureau of Mine defines Correlation Index (CI) as:

$$CI = \frac{48640}{T_b} + 473.7\gamma - 456.8 \tag{2.11}$$

where: T_b = Volume averaged boiling point.

CI of 0 to 15 indicates the sample to be paraffinic while greater than 50 indicate more of aromatic sample.[3]

2.3.11 Viscosity Index

Dean and Davis (1929) introduced the viscosity index (VI) by looking at the variations of viscosity and temperature of the samples. While several formulae are present to calculate VI based on different inputs, the most basic definition is given by Equation 2.12 below:

$$VI = \frac{L - U}{L - H} \times 100 \tag{2.12}$$

where: L = Kinematic viscosity of reference oil at 40^0C with 0 VI, cSt;U = Kinematic viscosity of oil whose VI is to be calculated at 40^0C with 0 VI, cSt; H = Kinematic viscosity of reference oil at 40^0C with 100 VI, cSt
The higher the VI, the more paraffinic the sample is.

The comparison between the aromaticity indicators are summarized in the Table 2.1. []

As mentioned already, these indicators are, most of the times, only qualitative. Sometimes, the values of the indicators will overlap between the hydrocarbon groups; see Figure 3.1. This creates subjectivity and hence uncertainity in determination of the aromaticity.

Table 2.1: Summary of the aromaticity indicators

Factor	Paraffins	Naphthens	Aromatics
Kw	high	medium	low
Ja	low	medium	high
Ya	low	medium	high
C_f	low	medium	high
VGC	high	medium	low
R_i	medium	low	high
m	low	medium	high
I	low	medium	high
CH	low	medium	high
CI	low	medium	high
VI	high	medium	low

There are other methods of characterization that were used in the early days of Petroleum industry; they were using monograms. They will use combination of available properties to obtain a property of interest. A good example is Winn Monogram which correlate API gravity (specific gravity), Kw, Mean average boiling point, molecular weight and aniline point for the petroleum fractions. The monogram is shown in Appendix C.2.

2.4 Critical Properties and Other EOS Parameters

Several correlations exist for finding the critical properties of the heptanes-plus fractions. The widely used ones are Lee-Kesler correlations, Riazi-Daubert and Cavett correlations. Most of these correlations depends on normal boiling point and specific gravity of the fraction. Similarly, acentric factor can be estimated using Kesler-Lee, Lee-Kesler, Edmister and other correlations using crtical properties and sometimes Kw as inputs.

Because most of the PNA characterization methods discussed in the next section have 'built in' critical properties and acentric factor calculations, the estimations methods mentioned earlier will not be discussed further in this work.

2.5 PNA Characterization Methods

Several methods have been proposed in estimation of the PNA content of the fractions. Four important methods will be discussed:

2.5.1 API (Riazi-Daubert) Methods[3]

The API method uses mass balance, Refractive intercepts and VGC to calculate the PNA composition of the fractions with the following equations:

$$\begin{bmatrix} 1 & 1 & 1 \\ 1.0482 & 1.038 & 1.081 \\ 0.744 & 0.915 & 1.04 \end{bmatrix} \begin{bmatrix} x_p \\ x_n \\ x_a \end{bmatrix} = \begin{bmatrix} 1 \\ R_i \\ VGC \end{bmatrix}$$

x_p, x_n and x_a above could mean weight fraction, mole fraction or simply volume fraction. This method can be used with fraction having molecular weights of 200-600.

The strength of this method is that it does not depend on properties that are overlapping for different types of the hydrocarbon families i.e. Ri and VGC. However, the greatest weakness is that it can't be used when the light fractions have kinematic viscosity of lower than 3.6cSt at 38^oC.

To account for the weakness, Riazi-Daubert introduced another factor: Viscosity gravity function (VGF) defined as:

$$VGF = -1.816 + 3.484\gamma - 0.1156 \times lnv_{38} \tag{2.13}$$

$$VGF = -1.948 + 3.535\gamma - 0.1613 \times lnv_{99} \tag{2.14}$$

where: $v_{38(100)}$ and $v_{99(210)}$ are kinematic viscosity in mm2/s (cSt) at 38^oC and 99^oC (100^oF and 210^oF) respectively.

Equation 2.13 and 2.14 above are derived from the fact that the plot of γ and $\ln(v)$ is linear for a particular hydrocarbon family, at a constant temperature.

With VGF in place of VGC, the new solutions of the simultaneous equations becomes:

For fractions with M$\leq$ 200

$$x_p = -13.359 + 14.4591R_i - 1.41344VGF \tag{2.15}$$

$$x_n = 23.9825 - 23.33304R_i + 0.81517VGF \tag{2.16}$$

$$x_a = 1 - x_n - x_p \tag{2.17}$$

For fractions with M$\geq$ 200

$$x_p = 2.5737 + 1.0133R_i - 3.573VGC \tag{2.18}$$

$$x_n = 2.464 - 3.6701R_i + 1.96312VGC \tag{2.19}$$

x_a is always calculated using equation 2.17.

Riazi-Daubert developed another method using other parameters when the one used above are not available. The new method use γ, m and CH ratio in the place of the unavailable quantity. The new solutions are:

For fractions with M$\leq$ 200

$$x_p = 2.57 - 2.877\gamma + 0.02876CH \tag{2.20}$$

$$x_n = 0.52641 - 0.7494x_p - 0.021811m \tag{2.21}$$

or

$$x_p = 3.7387 - 4.0829\gamma + 0.014772m \tag{2.22}$$

$$x_n = 1.5027 + 2.10152\gamma - 0.02388m \tag{2.23}$$

For fractions with M$\geq$ 200

$$x_p = 1.9842 - 0.27722R_i - 0.15643CH \tag{2.24}$$

$$x_n = 0.5977 - 0.761745R_i + 0.068048CH \tag{2.25}$$

or

$$x_p = 1.9382 + 0.074855m - 0.19966CH \tag{2.26}$$

$$x_n = -0.4226 - 0.00777m + 0.107625CH \tag{2.27}$$

When the aromatic content is high, Riazi-Daubert advise splitting the aromatic content into monoaromatics (monocyclic) (x_{ma}) and polyaromatics (polycyclic) (x_{pa}) for better accuracy. The split equations are:

$$x_{ma} = -62.8245 + 59.90816R_i - 0.0248335m \tag{2.28}$$

$$x_{pa} = 11.88175 - 11.2213R_i + 0.023745m \tag{2.29}$$

$$x_a = x_{ma} + x_{pa} \tag{2.30}$$

It is interesting to note that although Riazi-Daubert introduces splitting equations above, there is no indication that the aromatics used to develop their methodology contains polycyclic aromatic compounds.

For the conventional Petroleum PVT studies, most of the quantity used by API method are not measured. Hence there will be a big dependency on correlations to estimate the quantities to be used in the method. The other option is measuring these properties which may yet prove costly and time consuming. Another drawback with the method is that most of the equations used has been derived using volume contributions. Therefore, x_p, x_n and x_a are volume ratios; although the method developer's claims that they can be taken as molar or weight ratios with little errors.[3]

2.5.2 n-d-m Method

the n-d-m method use refractive index (n) at 20^{o}C, density (d) at 20^{o}C and molecular weight to find the PNA compositions. Strictly speaking, the method calculates the distribution of element carbon in each of the 3 families but since carbon is dominant element in all three families, it is assumed that the proportion of carbon represents the PNA distribution and that CH ratio is the same for all families. The error introduced by this estimation has been found to be within the measurement uncertainty of the PNA content.[3]

The method is based on the refractive index and specific gravities at 20^{o}C and 70^{o}C. The calculations in this method are as follows:[3]

$$\%C_A = av + 3660/M \tag{2.31}$$

$$\%C_N = \%C_R - \%C_A \tag{2.32}$$

$$\%C_p = 100 - \%C_R \tag{2.33}$$

with a $= \begin{cases} 430, & \text{if } v > 0 \\ 670, & \text{if } v < 0 \end{cases}$

The value of v is found using equation 2.35:

$$v = 2.51(n - 1.475) - (d - 0.851) \tag{2.34}$$

$$\%C_R = \begin{cases} 820w - 3 \times \%S + 10000/M, & \text{if } w > 0 \\ 1440w - 3 \times \%S + 10600/M, & \text{if } w < 0 \end{cases}$$

The value of w is given by:

$$w = (d - 0.851) - 1.11(n - 1.475) \tag{2.35}$$

This method requires Sulphur weight content (%S) not to exceed 2.06% and is only applicable with the fractions whose boiling point is above that of gasoline (308K to 473K). the n-d-m method can only be used with fractions having molecular weight greater than 200. Both conditions make n-d-m method suitable for C7+ characterization from SCN 15 and higher.

2.5.3 Bergman Method

Bergman has used mass balance, Kw and specific gravity to device his method. The method assumes all members of different hydrocarbon families will boil at the same temperature (realistic). This method gives PNA content as weight fractions. The method is as follows:[3,8]

$$w_a = 8.47 - K_w \tag{2.36}$$

$$w_p + w_n = 1 - w_a \tag{2.37}$$

$$\frac{w_p}{\gamma_p} + \frac{w_n}{\gamma_n} = \frac{1}{\gamma} - \frac{w_a}{\gamma_a} \tag{2.38}$$

The specific gravity for each of the family are calculated using equation below:

$$\gamma_i = \sum_{n=0}^{3} A_n (T_b - 460)^n \tag{2.39}$$

where i stands for p, n or a. The values of A_n for every hydrocarboon family are shown in Appendix B.2. T_b in all Bergmans' equations are in ^{o}R.

Similarly the values of Critical temperature (^{o}R) and critical pressure (psia) are given by Equation 2.40 and 2.41 respectively:

$$T_{ci} = \sum_{n=0}^{3} B_n (T_b - 460)^n \tag{2.40}$$

$$P_{ci} = \sum_{n=0}^{3} C_n (T_b - 460)^n \tag{2.41}$$

The values of B_n and C_n for every hydrocarboon family are also shown in Appendix B.2.

Acentric factor (ω) for every family are given by Equation 2.42, 2.43 and 2.44 below:

$$\omega_p = 0.14 + 0.0009(T_b - 460) + 0.233 \times 10^{-6}(T_b - 460)^2 \tag{2.42}$$

$$\omega_n = \omega_p - 0.075 \tag{2.43}$$

$$\omega_a = \omega_p - 0.1 \tag{2.44}$$

When boiling point and specific gravity of the cuts are not available, Silva and Rodriguez[3] have recommended using Equations 2.45 and 2.46 below:

$$T_b = 447.08723 \times ln(\frac{M}{64.2576}) + 460 \tag{2.45}$$

$$\gamma = 0.132467 \times ln(T_b - 460) + 0.0116483 \tag{2.46}$$

T_b is in ^{o}R for all equations in Bergman method

Bergman method may results in negative compositions, so he imposed equation D.8 and D.9 as conditions on the solutions:

$$0.03 \geq w_a \leq 0.35 \tag{2.47}$$

$$w_p \geq 0.2 \tag{2.48}$$

2.5.4 Robinson-Peng Method

Robinson and Peng (1972) gave another complete C7+ characterization based on the PNA content. Like Bergman, their method also includes the estimation of critical properties and other EOS parameter. They have based their method on mass balance, molecular weight and boiling point:[9,8]

$$\begin{bmatrix} 1 & 1 & 1 \\ M_pT_{bp} & M_nT_{bn} & M_aT_{ba} \\ M_p & M_n & M_a \end{bmatrix} \begin{bmatrix} x_p \\ x_n \\ x_a \end{bmatrix} = \begin{bmatrix} 1 \\ M \times WABP \\ M \end{bmatrix}$$

Where: WABP = weighted averaged boiling point of each cut.

The normal boiling points for all families given by Equation 2.49.

$$ln(T_b) = \sum_{i=1}^{6} C_i(n-6)^{i-1} \tag{2.49}$$

Ci are given in the Appendix B.3.

The molecular weights of each carbon number are calculated using Equations 2.50, 2.51 and 2.52 for paraffinic, naphthenic and aromatic fraction respectively

$$M_p = 14.026n + 2.016 \tag{2.50}$$

$$M_p = 14.026n - 14.026 \tag{2.51}$$

$$M_p = 14.026n - 20.074 \tag{2.52}$$

where n is the single carbon number of interest

The critical pressure (atm), critical temperature (K) and acentric factor for each of the family can be calculated using the equation 2.53, 2.54 and 2.55 respectively.

$$P_c = \frac{14.026n + \gamma}{(0.227n + \beta)^2} \tag{2.53}$$

$$T_c = S \times T_b \times [1 + \frac{3log(P_c)}{7(1+\omega)}] \tag{2.54}$$

$$\omega = f \times n + g \tag{2.55}$$

The constants γ, β, f and g are given in the Appendix B.3 for all hydrocarbon groups.

The correction term S is given by Equation 2.56 below:

$$S = 0.996704 + 0.0043155n \tag{2.56}$$

Robinson and Peng method estimate Binary interaction parameters (k) using equation 2.57 below

$$k = 0.379642 + 1.48503\omega - 0.164423\omega^2 + 0.016666\omega^3 \tag{2.57}$$

Liquid Molar volumes are estimated using Equation 2.58 below:

$$v = a \times n + b \tag{2.58}$$

Constants a and b for PNA are given in the Appendix B.3.

Robinson-Peng has put the conditions that the paraffinic content cannot exceeds 90%.

Chapter 3

Challenges and The Proposed Solutions With The Existing Methods

While the methods described above have been used extensively, they suffer from different weaknesses. This chapter will discuss the challenges and the proposed solutions.

3.1 Challenges

3.1.1 Absence of Relevant Data

The use of some of these procedure will require extra information that are not available with the conventional lab PVT report. For example, the API method will require viscosity measurements at different temperatures; n-d-m method requires refractive index; WABP for Robinson-Peng. This will require extra type of measurements which might be both time consuming and expensive.

3.1.2 Ignoring Other Type of Compounds That May Exist

With the definitions of PNA as given in the *Introduction*, all existing methods ignore other type of compounds that exist in petroleum fluids. For instance, all methods ignore the iso (branched) paraffins and polycylic compounds in their definitions. The effect of this will be discussed later.

3.1.3 Use of Non-Exclusive Quantities

Some of these methods use quantities that are not exclusive for each of the hydrocarbon family. For example, Bergman use a qualitative Watson characterization factor to estimate the weight fraction of the aromatics. Refering to Figure 3.1, it is clear that even a pure naphthenic compound could have aromatic weight component if Bergman method is used due to overlapping of the Kw.

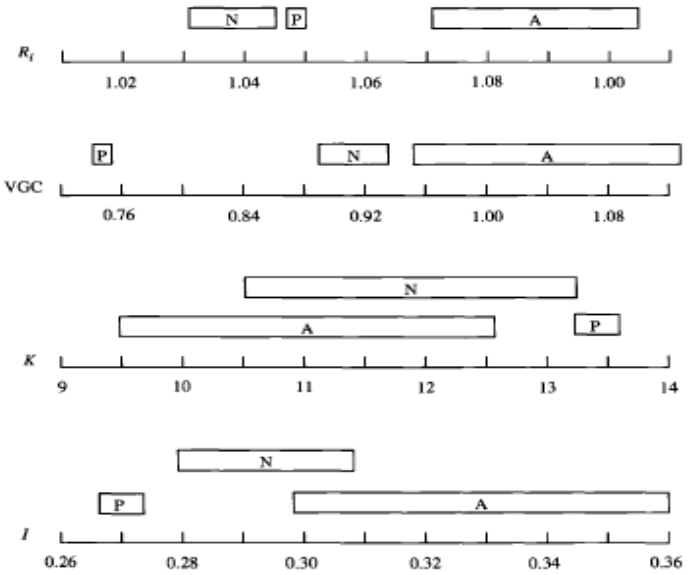

Figure 3.1: Overlapping of the PNA indicators[3]

3.1.4 Standard Conditions Definition

While the Petroleum industry use 15.56^{o}C as standard temperature, the process engineering world use 20^{o}C as such. This creates some inconsistency, and hence will introduce extra work whenever some of the procedures are used. For example, the densities from API method and n-d-m method use 20^{o}C as reference temperature. A petroleum engineer working with these methods must have extra procedure of changing these quantities to desirable temperatures before working with them.

3.1.5 Density Conservations

Using Bergman and, Robinson and Peng methods on Katz-Firoozabadi C7+ general data, both methods have been found by the author not to honour fractions' densities. Using the compositions obtained from these methods and the desnities of each family

group (for each SCN as given by the methods themselves); the resultant "average" densities were calculated and have been found to be underestimated as shown by Figure 3.2. Combination of Hopke and Lee, and Bergman correction severely overestimate the densities.

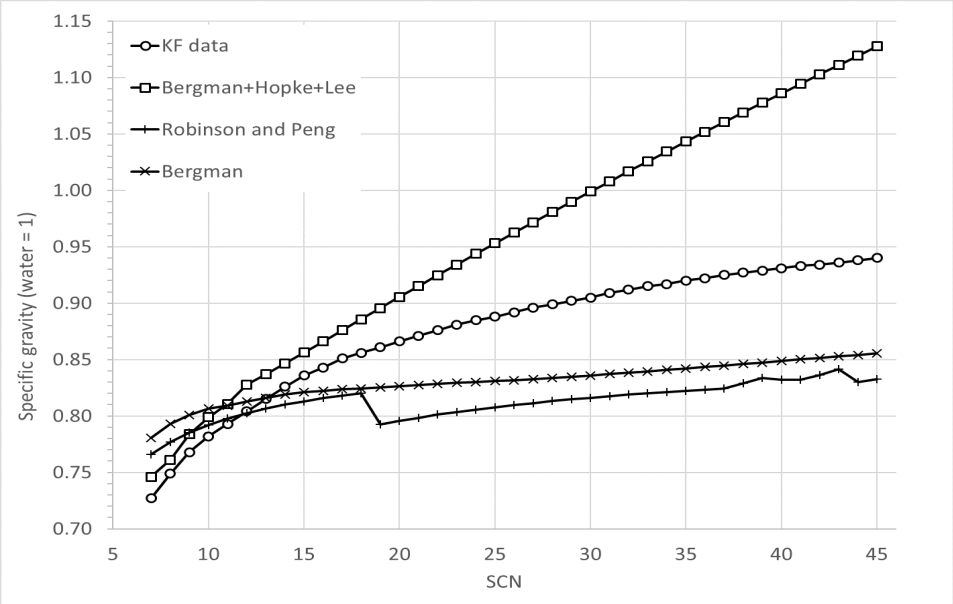

Figure 3.2: Resultant average specific gravity vs KF specific gravity

When the P-N-A densities are plotted against the KF data, the problem of definitions of the compounds becomes clear. Figure 3.3 shows the densities of paraffin, naphthenic and aromatics for SCN 6-45.

With the averaging techniques normally used, it is very difficult to reproduce the KF densities using the compositions and P-N-A densities since there are no specific gravity values greater than KF data from SCN 18.

3.1.6 Negative Solutions

These methods often lead to negative compositions or greater than unity compositions. For example, Whitson[1] have shown that for RP method, there is very small window to work with for each fraction so as to avoid the negative and greater than unity compositions. The higher the fraction interms of boiling point (SCN), the smaller the window to work with as shown by Figure 3.4 below:

Each method tries to come up with the procedure to be followed when this type of situation arises. However, even then, some of these conditions are not complete. For example, Robinson and Peng have proposed that the paraffinic content to be trimmed to 90% whenever it goes beyond it. However, the method do not instructs on the distribution of the remaining 10% between the aromatics and naphthenic fractions.

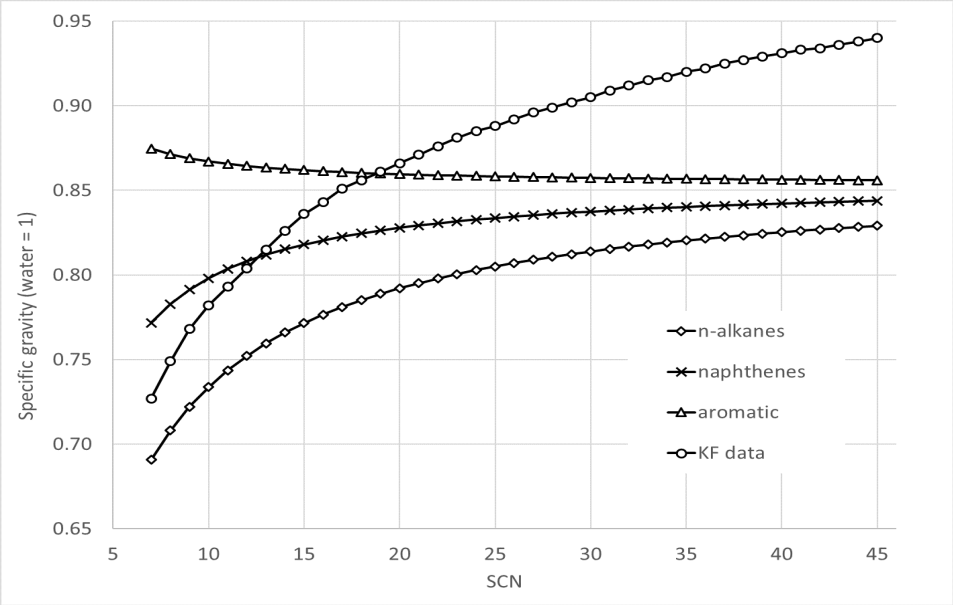

Figure 3.3: PNA densities vs KF data

3.1.7 SCN Definition Agreement

With the definitions of the PNA compounds given in the *Introduction* the classic definition of the SCN i.e. normal to normal paraffin, is violated after few carbon numbers. For example, the Robinson-Peng method will violate definition starting at SCN 21.

3.2 Proposed Solutions

It is important to note that the solutions proposed and even the work of this thesis will be based on the Robinson-Peng method and the KF data as the basis. However, the solutions, with modifications, can be extended to other methods. Solutions of some key shortcoming will be discussed here that formed the basis of this work:

3.2.1 Absence of Relevant Data

A procedure will be produced where the conventional laboratory PVT measurement will be enough to characterize the PNA content. Since the conventional laboratory report will normally give out molecular weight and densities of the fractions; the new method will use mass balance, molecular weight and liquid molar volumes (combination of the molecular weight and the density) as the inputs. The new method (using same definitions of aromatics) and the original Robinson and Peng method gives relatively

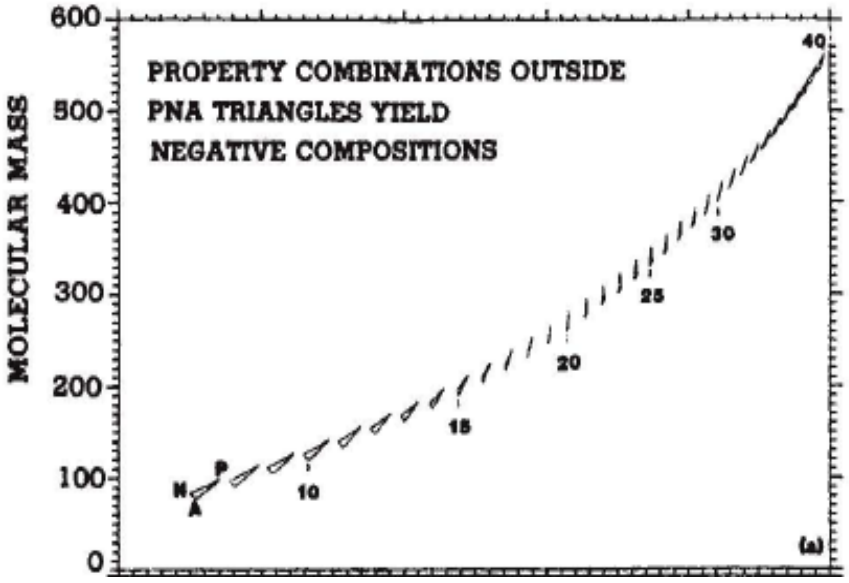

Figure 3.4: Working windows for positive solutions of the Robinson-Peng Method[1]

similar composition results. Using the PNA compositions obtained and the densities for each family, the averaged density for each SCN are as shown by Figure 3.5.

3.2.2 Ignoring Other Type of Compounds

The Robinson-Peng equations will be checked for consistency against other compounds in each of the family group. For example, the equations used to calculate molar liquid volumes and molecular weights will be checked against iso-parrafins for the paraffinic family and polycyclic compounds and isocyclic compounds for the naphthenic and aromatic families. The definitions of PNA compounds will then be modified accordingly to reflect the presence of other compounds should the need be seen.

3.2.3 Using Non-Exclusive Quantities

Using molar volume and molecular weight (density) will solve the problem of using the overlapping quantities between the three families. While this problem is particularly problematic with the use of Kw in Bergman method, the densities of PNA compounds do not overlap as seen in Figure 3.3, and hence molar volumes can be used successfully to solve the exclusivity.

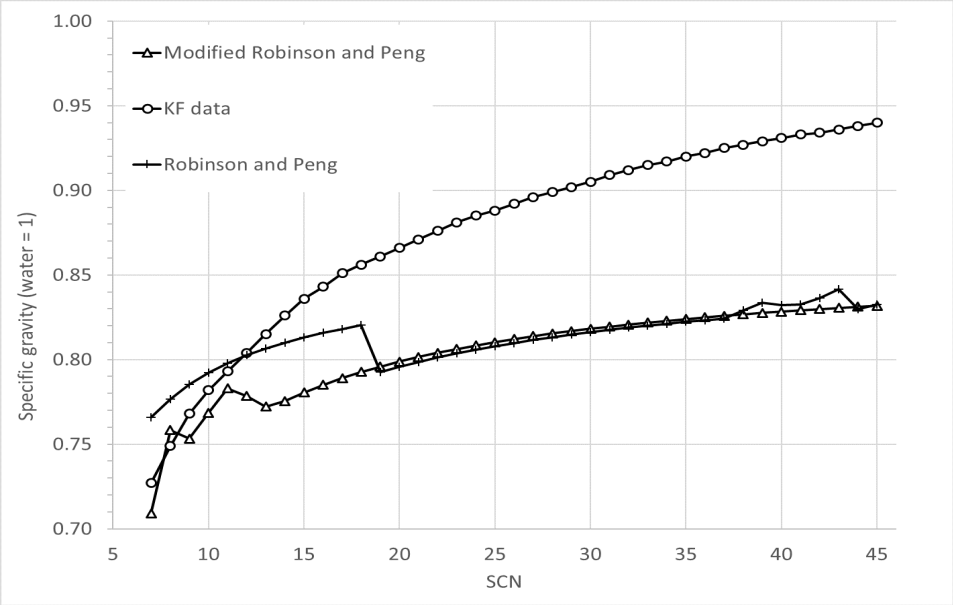

Figure 3.5: Comparison of Robinson and Peng and Modified Robinson and Peng densities

3.2.4 Standard Conditions

Since the acceptable solution for both petroleum and chemical engineering disciplines is far from being agreed upon, this work will honour the petroleum engineering tradition of defining standard temperature as 15.56^{o}C Since the other shortcomings are rather the product of the methodology itself, they will be discussed in detail in the discussion section of the report.

Chapter 4

Developing Correlations

Checking the consistency of the RP equations

Using Equation 2.49 to compare the boiling points of the PNA compounds with the values found in the literature, it was found that there is very good match between the values given by correlations and those given in literatures. The absolute average deviations (AAD) for the Parrafins, napthenes and aromatics were 0.95K, 1.89K and 0.68K respectively. However, including other compounds not considered in the definitions, it was found that the AAD were 5.12K, 3.27K and 7.51K for the Parrafinic, naphthenic and aromatic family respectively.

Using Equation 2.58 to find liquid molar volume and comparing the values with those calculated using molecular weights and densities found in the literature, the densities AAD were found to be $0.65g/cm^3$, $0.65g/cm^3$ and $0.35g/cm^3$ for the paraffinic, naphthenic and aromatics compounds respectively. However, including the excluded compounds for each of the family, the AAD were $1.18g/cm^3$, $1.86cg/cm^3$ and $6.68g/cm^3$ respectively. Similar results are obtained if density is considered.

The above results show that when other compounds are included in the definitions, aromatics boiling point and molar volume are affected the most. This fact and (considering) the shape of the aromatic trendline in Figure 3.3 warrant a new definition of the aromatic component of the PNA.

It was also noted that the assumptions of Robinson-Peng (and other) method that with each successive SCN, a single carbon is added to the normal paraffinic chain of napthenes and aromatic compounds is reasonable with their equations. However, with the introduction of new compounds the assumption is significantly affected. This is especially true with the aromatic compounds; which gives another reason of changing the definition of the aromatics in the PNA characterization.

4.1 New Aromatics Definition

Due to the problem discussed above, new correlations of molecular weight (similar to Equation 2.52) and molar volume (similar to Equation 2.58.) were searched for the new characterization methodology. For each SCN, denser aromatic compounds than those assumed in the Robinson-Peng methodology were searched in the literature,[10],[11].[12] All dense compounds were placed in appropriate SCN definition according to their boiling points. The identified compounds were plotted in Figure 4.1:

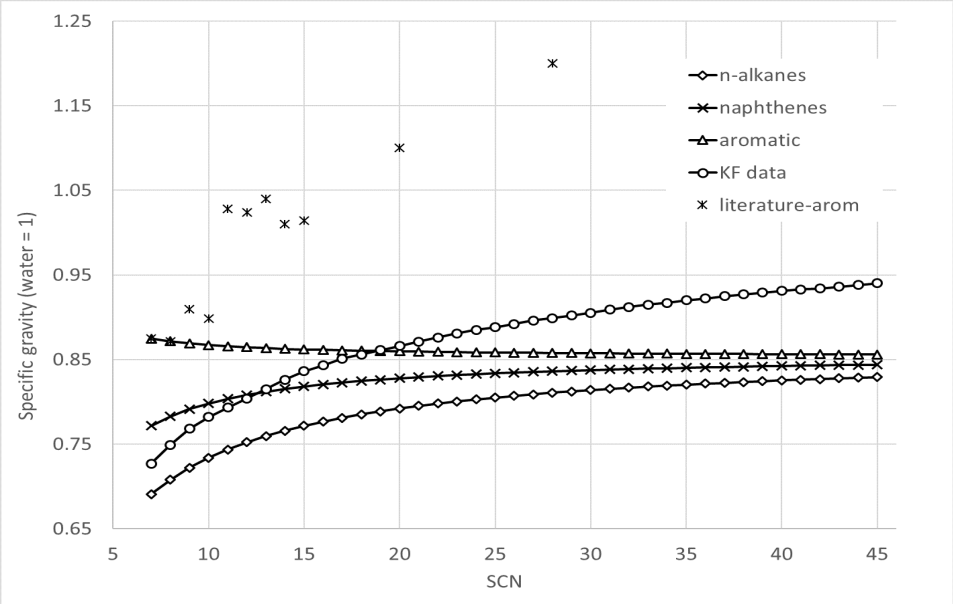

Figure 4.1: Densities of poly-cyclic aromatic compounds from literature against classic aromatic definition.

Two methods showed reasonable results:

i Choosing the heaviest compound in each SCN and use their properties in characterization

ii Finding averages properties for all compounds in each SCN

Both methods were applied to KF data; the resulting PNA distribution were used to re-calculate the densities of each SCN, the results are as shown by Figure 4.2:

Figure 4.2 shows that choosing the heaviest compounds for the new characterization conserve the density better and hence was chosen as the new characterization method. The conditions imposed by Bergman were more complete and produced better density conservation and were therefore used in the new characterization. For method (ii) characterization, see Appendix D.

When similar approach was used for molecular weights, all methods show good averaged molecular weights as seen in Figure 4.3

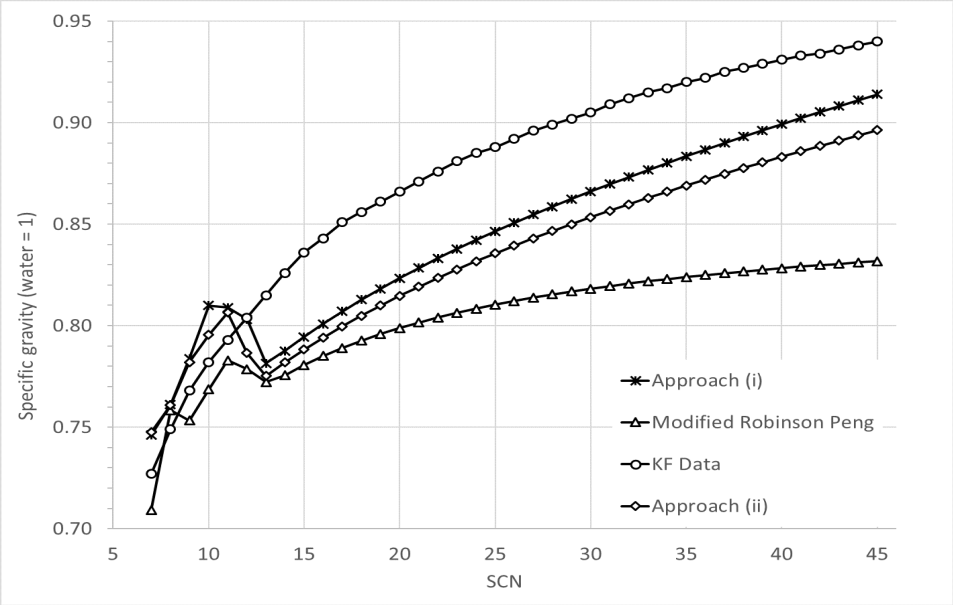

Figure 4.2: Comparison of Method (i) and Method (ii)

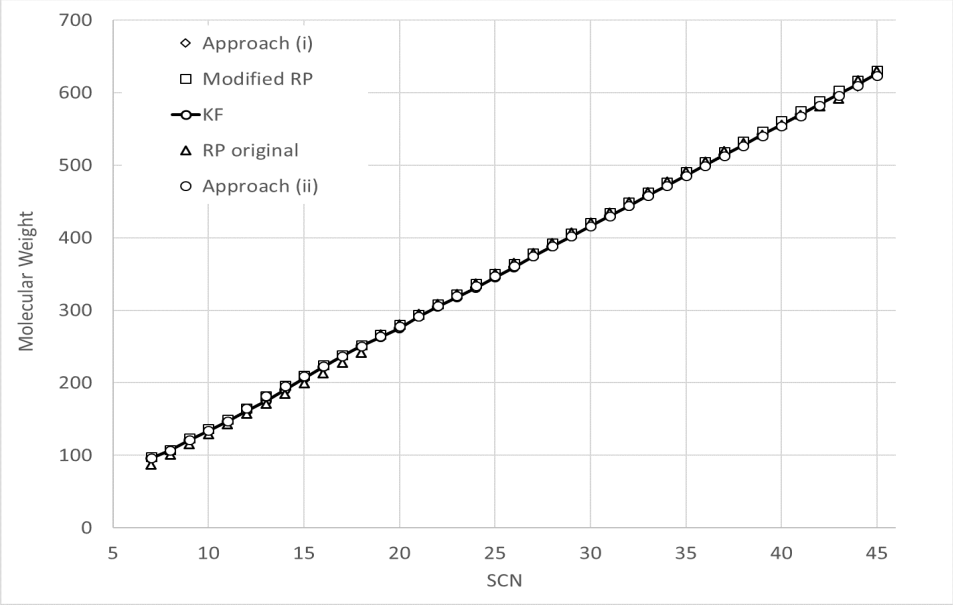

Figure 4.3: Comparison of average molecular weights for different approaches

4.2 Properties Correlations

Several properties correlations from Robinson and Peng method were developed (re-tuned) so as to be used in the new characterization. Since the definitions of paraffinic and naphthenic compounds remained unchanged, only correlations of the aromatics were

re-tuned.

4.2.1 Aromatic Molecular Weight

Molecular weights of the selected aromatic compounds were fitted for selected compounds as seen in the Figure 4.4

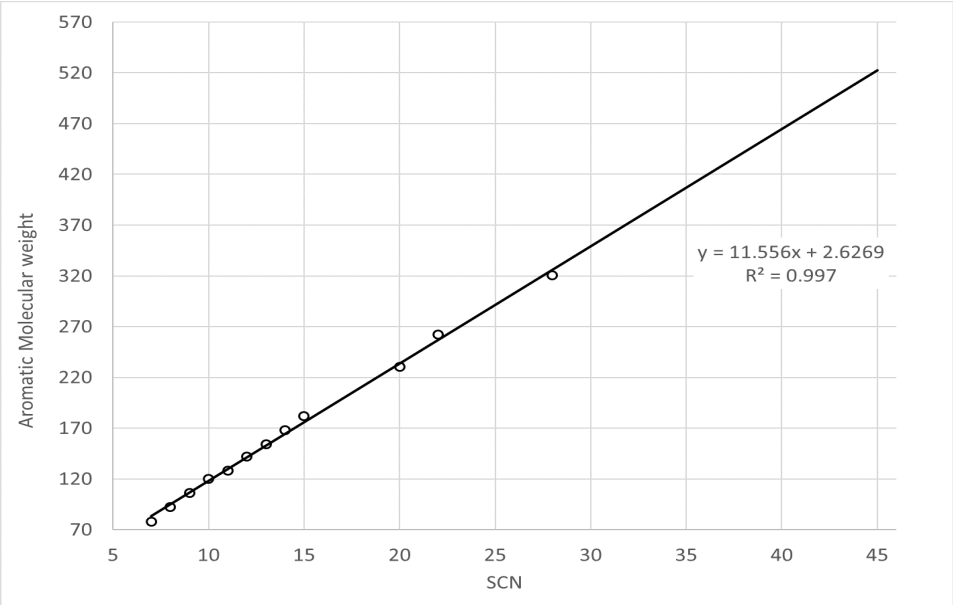

Figure 4.4: New aromatic molecular weights vs SCN

4.2.2 Liquid Molar Volume

In similar fashion, liquid molar volumes were fitted and the results are summarized by Figure 4.5.

Using the new aromatic molar volume definition, the densities for the KF, paraffinic, naphthenic and aromatics are shown by Figure 4.6.

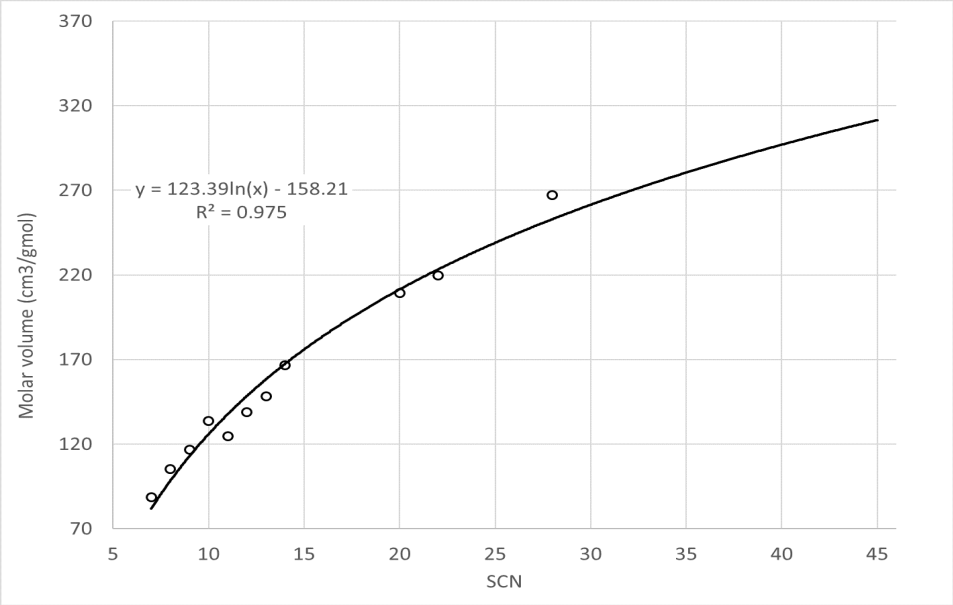

Figure 4.5: New aromatic molar volume vs SCN

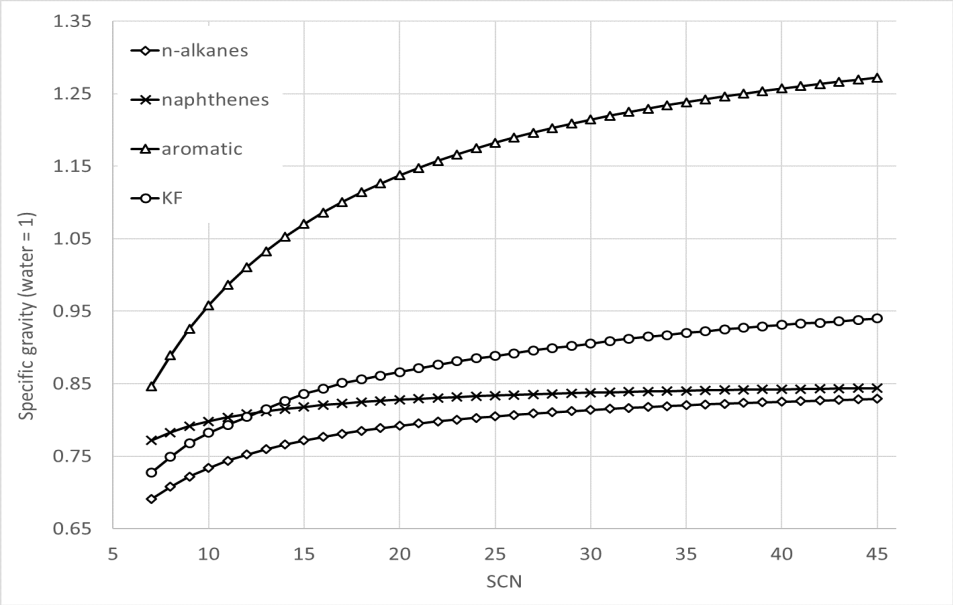

Figure 4.6: New PNA and KF specific gravities using new aromatic definitions

While the modified Robinson-Peng characterization fails to observe ideal molar volume mixing at SCN 26, the new molar volume correlation ensures that ideal mixing is possible for all SCN.

4.2.3 Boiling Point

Boiling point correlation was developed to be used in the calculation of critical pressures. It can also be used in the Robinson Peng original characterization method when the boiling points data are available.

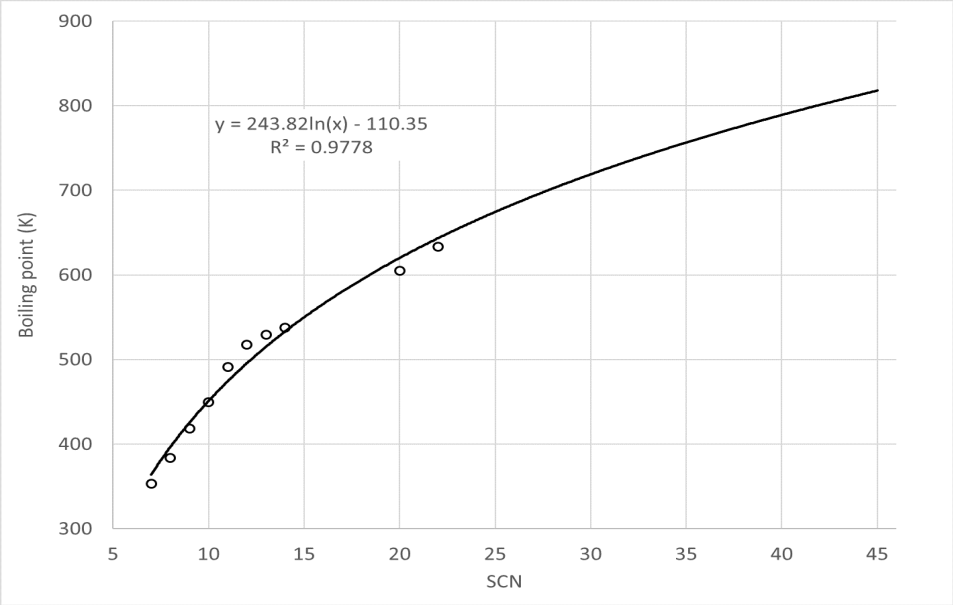

Figure 4.7: Aromatic BP vs SCN

The new boiling point correlations improves on the problem in Section 3.1.6 i.e. consistency with the SCN definition. While the existing methods fails to observe the definition from SCN 21, the proposed method start to have problems at the SCN 27.

4.2.4 Acentric Factor

Another important property correlated was the acentric factor and the results are shown in the Figure 4.8.

4.2.5 Critical Temperature

Equation 2.54 used to calculate the critical temperatures with the gamma and beta values changed to 3622.5 and 7.9 respectively

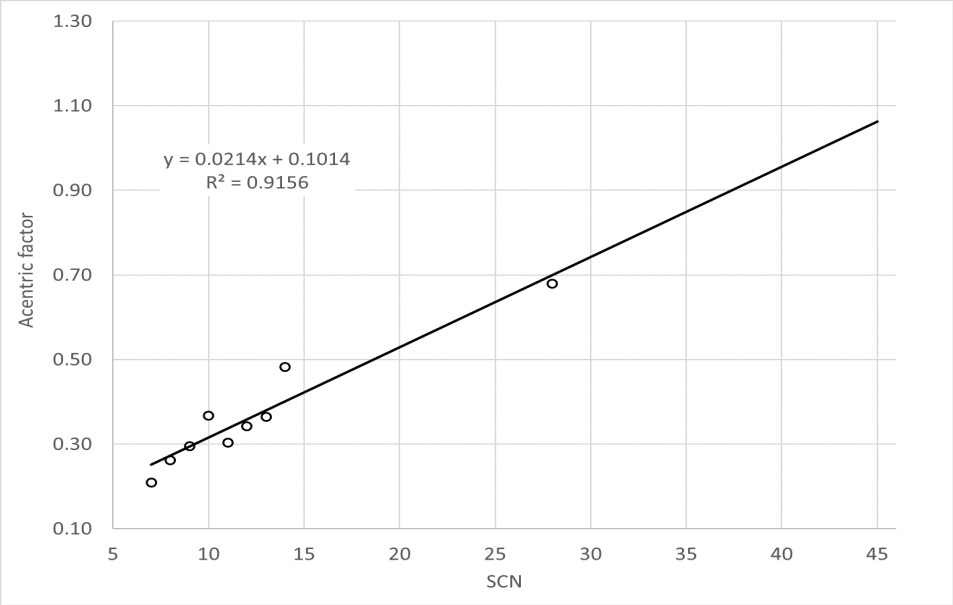

Figure 4.8: Aromatic AF vs SCN

4.2.6 Critical Pressure

Equation 2.53 is used to find critical pressures for each single carbon number. However, the correction term s is now calculated using Equation 4.1.

$$S = 0.976333 + 0.0025189n \tag{4.1}$$

4.2.7 Binary Interaction Parameters

The binary interaction parameters was not correlated due to the unavailability of the data. The fact that BIPS are used as the EOS tuning parameter in EOS modelling further make BIPS correlation of little significance. As a starting point, the BIPS given by Robinson-Peng,[9] Nagy and Shirkovskiy, and, Reid *et al.* could be used[5] with an appropriate EOS.

4.2.8 PNA Composition Corrections

Like other methods, the proposed characterization does give negative solutions. However, using KF data, it was found that the new method significantly improves the values obtained.

Nevertheless, corrections for the obtained solution is necessary. Bergman, Hopke and Lee, and Robinson and Peng were both applied to the new method despite all being

consistent with each other.

The Bergman corrections were found to be most accurate in conserving the density and hence will be used. The Bergman correction, also, has the advantage over other corrections since it gives the correction for all PNA constituents.

Chapter 5

Application Of The New Method

To apply the new characterization method, molecular weights and densities of each SCN should be available. The following steps should then be followed:

STEP 1: Find MW and liquid molar volume for every PNA compounds. Calculate specific volumes for the PNA families using Equation 5.1, 5.2 and 5.3 respectively.

$$v_p = 14.026n - 14.026 \tag{5.1}$$

$$v_n = 16.280n + 31.102 \tag{5.2}$$

$$v_a = 123.39 \times ln(n) - 158.21 \tag{5.3}$$

The molecular weights for paraffinic, naphthenic and aromatics are calculated using equations 5.4, 5.5 and 5.6 respectively.

$$M_p = 14.026n + 2.016 \tag{5.4}$$

$$M_n = 14.026n - 14.016 \tag{5.5}$$

$$M_a = 11.556n - 2.627 \tag{5.6}$$

STEP 2: Solve the following simultaneous equations:

$$\begin{bmatrix} 1 & 1 & 1 \\ v_p & v_n & v_a \\ M_p & M_n & M_a \end{bmatrix} \begin{bmatrix} x_p \\ x_n \\ x_a \end{bmatrix} = \begin{bmatrix} 1 \\ v \\ M \end{bmatrix}$$

The fraction molar volume should be calculated from MW and density of each fraction

STEP 3: change the molar composition to weight composition:

$$w_i = \frac{x_i \times M_n}{M_i} \tag{5.7}$$

Where i stand for p,n or A and M_n is molecular weight of SCN in question.

STEP 4: Apply Bergman corrections:

$$0.03 \geq w_a \leq 0.35 \tag{5.8}$$

$$w_p \geq 0.2 \tag{5.9}$$

STEP 5: change weight compositions to molar compositions:

$$x_i = \frac{w_i \times M_i}{M_n} \tag{5.10}$$

STEP 6: Calculate boiling points (K) for PNA fractions:

$$T_{bp} = 251.19ln(n) - 132.07 \tag{5.11}$$

$$T_{bn} = 260.14ln(n) - 165.26 \tag{5.12}$$

$$T_{ba} = 123.39ln(n) - 158.21 \tag{5.13}$$

STEP 7: calculate Critical pressures (atm)

$$P_{cp} = \frac{14.026n + 2.016}{(0.227n + 0.340)^2} \tag{5.14}$$

$$P_{cn} = \frac{14.026n}{(0.227n + 0.090)^2} \tag{5.15}$$

$$P_{ca} = \frac{14.026n + 3622.5}{(0.227n + 7.9)^2} \tag{5.16}$$

STEP 8: Calculate Acentric factor

$$\omega_p = 0.0432n + 0.0457 \tag{5.17}$$

$$\omega_n = 0.0432n - 0.0448 \tag{5.18}$$

$$\omega_a = 0.0214n + 0.1014 \tag{5.19}$$

STEP 9: Calculate Critical temperatures (K) for all families using equation 5.20

$$T_c = S \times T_b \times [1 + \frac{3log(P_c)}{7(1 + \omega)}] \tag{5.20}$$

The correction term S for Paraffinic and naphthenic is given by equation 5.21 and for aromatics equation 5.22.

$$S = 0.996704 + 0.0043155n \tag{5.21}$$

$$S = 0.976333 + 0.0025189n \tag{5.22}$$

Although this method is based on the Robinson and Peng method, some of the equations have been re-written/re-tuned to be user friendly.

Chapter 6

Conclusion

It has been shown that the new method improves the density conservation significantly while reducing the severity of negative compositions. The new characterization method also helps to solve or at least improves on many other problems that were present with the existing methods.

However, despite its improvements, the method is based on data sets that are not complete but only those that could be found in the literature. Although the method includes poly-cyclic aromatics in its definition, yet it leaves other aromatic compounds that are expected to be found. As discussed before, averaging all aromatics in defining aromatics improves on the Robinson and Peng method, yet it has poor density conservation compared to the proposed method. Nevertheless, it is reasonable to assume that the proposed method has built in average properties since there are other compounds that have not been well catalogued.

The following can be done to further fine-tune the method

i Test the new methodology on more laboratory data with known PNA content

ii Test the new methodology on laboratory synthetic mixture

iii Performing Gas Chromatography-Mass Spectroscopy (GC-MS) to oil samples. The GC-MS gives the PNA distribution for each SCN. Gas Chromatography-Mass Spectroscopy-Infrared (GC-MS-IR) may give individual compounds that have been catalogued in the manufacturer library to further increase the knowledge on the compositions.

Despite, the "straight forward" looking point iii above in PNA characterization, the method will require extra time and effort from laboratory. Even if the technique is used, there is no guarantee in identifying all compounds present since only those catalogued in the manufacturer's library will be identified. Even if all or most compounds are identified, a lumping methodology have to be developed before they can be accurately used in the EOS.

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Appendix A

Katz Firoozabadi C7+ Characterization

Table A.1: Katz-Firoozabadi heptanes-plus characterization[5]

	Katz-Firoozabadi Generalized Properties							Lee-Kesler-Plöcker-Knapp-Lee[1] Correlations				
	T_b Interval*		Average T_b									
Fraction Number	Lower (°F)	Upper (°F)	(°F)	(°R)	γ*	M	Defined K_w	T_c (°R)	p_c (psia)	ω	Riazi[1] V_c (ft³/lbm mol)	Defined Z_c
6	97.7	156.7	147.0	606.7	0.690	84	12.27	914	476	0.271	5.6	0.273
7	156.7	210.0	197.4	657.1	0.727	96	11.96	976	457	0.310	6.2	0.272
8	210.0	259.0	242.1	701.7	0.749	107	11.86	1,027	428	0.349	6.9	0.269
9	259.0	304.3	288.0	747.6	0.768	121	11.82	1,077	397	0.392	7.7	0.266
10	304.3	346.3	330.4	790.1	0.782	134	11.82	1,120	367	0.437	8.6	0.262
11	346.3	385.5	369.0	828.6	0.793	147	11.84	1,158	341	0.479	9.4	0.257
12	385.5	422.2	406.9	866.6	0.804	161	11.86	1,195	318	0.523	10.2	0.253
13	422.2	456.6	441.0	900.6	0.815	175	11.85	1,228	301	0.561	10.9	0.249
14	456.6	489.0	475.5	935.2	0.826	190	11.84	1,261	284	0.601	11.7	0.245
15	489.0	520.0	510.8	970.5	0.836	206	11.84	1,294	268	0.644	12.5	0.241
16	520.0	548.6	541.4	1,001.1	0.843	222	11.87	1,321	253	0.684	13.3	0.236
17	548.6	577.4	572.0	1,031.7	0.851	237	11.87	1,349	240	0.723	14.0	0.232
18	577.4	602.6	595.4	1,055.1	0.856	251	11.89	1,369	230	0.754	14.6	0.229
19	602.6	627.8	617.0	1,076.7	0.861	263	11.90	1,388	221	0.784	15.2	0.226
20	627.8	651.2	640.4	1,100.1	0.866	275	11.92	1,408	212	0.816	15.9	0.222
21	651.2	674.6	663.8	1,123.5	0.871	291	11.94	1,428	203	0.849	16.5	0.219
22	674.6	692.6	685.4	1,145.1	0.876	305	11.94	1,447	195	0.879	17.1	0.215
23	692.6	717.8	707.0	1,166.7	0.881	318	11.95	1,466	188	0.909	17.7	0.212
24	717.8	737.6	726.8	1,186.5	0.885	331	11.96	1,482	182	0.936	18.3	0.209
25	737.6	755.6	746.6	1,206.3	0.888	345	11.99	1,498	175	0.965	18.9	0.206
26	755.6	775.4	766.4	1,226.1	0.892	359	12.00	1,515	168	0.992	19.5	0.203
27	775.4	793.4	786.2	1,245.9	0.896	374	12.01	1,531	163	1.019	20.1	0.199
28	793.4	809.6	804.2	1,263.9	0.899	388	12.03	1,545	157	1.044	20.7	0.196
29	809.6	825.8	820.4	1,280.1	0.902	402	12.04	1,559	152	1.065	21.3	0.194
30	825.8	842.0	834.8	1,294.5	0.905	416	12.04	1,571	149	1.084	21.7	0.191
31	842.0	858.2	851.0	1,310.7	0.909	430	12.04	1,584	145	1.104	22.2	0.189
32	858.2	874.4	865.4	1,325.1	0.912	444	12.04	1,596	141	1.122	22.7	0.187
33	874.4	888.8	879.8	1,339.5	0.915	458	12.05	1,608	138	1.141	23.1	0.185
34	888.8	901.4	892.4	1,352.1	0.917	472	12.06	1,618	135	1.157	23.5	0.183
35	901.4	915.8	906.8	1,366.5	0.920	486	12.06	1,630	131	1.175	24.0	0.180
36			919.4	1,379.1	0.922	500	12.07	1,640	128	1.192	24.5	0.178
37			932.0	1,391.7	0.925	514	12.07	1,650	126	1.207	24.9	0.176
38			946.4	1,406.1	0.927	528	12.09	1,661	122	1.226	25.4	0.174
39			959.0	1,418.7	0.929	542	12.10	1,671	119	1.242	25.8	0.172
40			971.6	1,431.3	0.931	556	12.10	1,681	116	1.258	26.3	0.170
41			982.4	1,442.1	0.933	570	12.11	1,690	114	1.272	26.7	0.168
42			993.2	1,452.9	0.934	584	12.13	1,697	112	1.287	27.1	0.166
43			1,004.0	1,463.7	0.936	598	12.13	1,706	109	1.300	27.5	0.164
44			1,016.6	1,476.3	0.938	612	12.14	1,716	107	1.316	27.9	0.162
45			1,027.4	1,487.1	0.940	626	12.14	1,724	105	1.328	28.3	0.160

*At 1 atmosphere.
**Water = 1.

Appendix B

Constants

B.1 Yarbourough Constants

Table B.1: Yarbourough constants[2]

Ya	A_o	A_1	A_2	A_3
0.0	-7.42855×10^{-2}	-1.72341	1.38058×10^{-3}	-3.34169×10^{-2}
0.1	-4.25800×10^{-1}	-7.00017×10^{-1}	-3.30947×10^{-5}	-8.65465×10^{-2}
0.2	-4.47553×10^{-1}	-7.65111×10^{-1}	1.77982×10^{-4}	-1.07746×10^{-1}
0.3	-4.39105×10^{-1}	-9.44068×10^{-1}	4.93708×10^{-4}	-1.19267×10^{-1}
0.4	-2.73719×10^{-1}	-1.39960	3.80564×10^{-3}	-5.92005×10^{-2}
0.6	-7.39412×10^{-3}	-1.97063	5.87273×10^{-3}	-1.67141×10^{-2}
0.8	-3.17618×10^{-1}	-7.78432×10^{-1}	2.58616×10^{-3}	-1.08382×10^{-3}

B.2 Bergman Constants

Table B.2: Constants for the Bergman Characterization[8]

Constant	Paraffins	Naphthenes	Aromatics
A_o	0.582486	0.694208	0.916103
A_1	0.00069481	0.0004909267	0.000250418
A_2	$-0.7572818 \times 10^{-6}$	-0.659746×10^{-6}	0.357967×10^{-6}
A_3	0.3207736×10^{-9}	0.330966×10^{-9}	-0.166318×10^{-6}
B_O	275.23	156.8906	289.535
B_1	1.2061	2.6077	1.7017
B_2	-0.00032984	-0.003801	-0.0015843
B_3	0	0.2544×10^{-5}	0.82358×10^{-6}
C_O	573.011	726.414	1184.514
C_1	–1.13707	–1.3275	–3.44681
C_2	0.00131625	0.0009846	0.0045312
C_3	-0.85103×10^{-6}	-0.45169×10^{-6}	-0.23416×10^{-6}

B.3 Robinson and Peng Constants

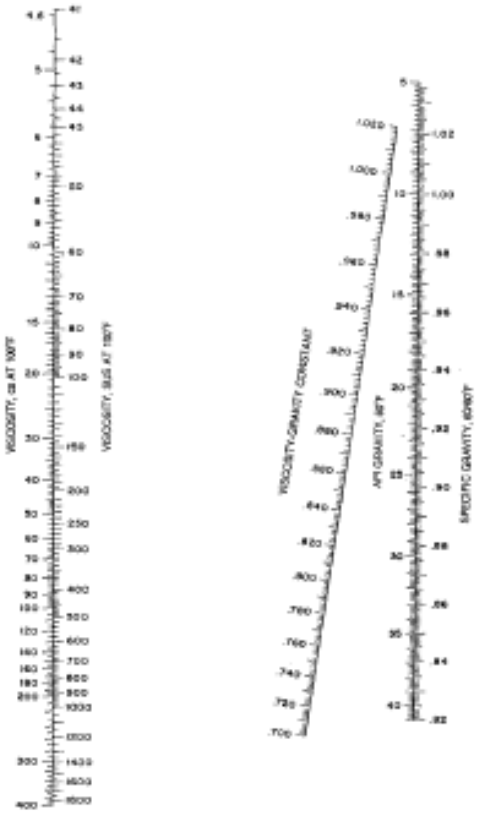
Table B.3: Constants for the Robinson and Peng Characterization[9]

Constant	Paraffins	Naphthenes	Aromatics
a	16.2801	16.3762	16.4383
b	31.1016	10.7918	-9.3314
C_1	5.8345183	5.8579332	5.8671760
C_2	$0.84909035 \times 10^{-1}$	$0.79805995 \times 10^{-1}$	$0.80436947 \times 10^{-1}$
C_3	$-0.52635428 \times 10^{-2}$	$-0.43098101 \times 10^{-2}$	$-0.47136506 \times 10^{-2}$
C_4	0.2125908×10^{-3}	$0.14783123 \times 10^{-3}$	$0.18233365 \times 10^{-3}$
C_5	$-0.44933363 \times 10^{-5}$	$-0.27095216 \times 10^{-5}$	$-0.38327239 \times 10^{-5}$
C_6	$0.37285365 \times 10^{-7}$	$0.19907794 \times 10^{-7}$	$0.32550576 \times 10^{-7}$
f	0.0432	0.0432	0.0445
g	0.0457	-0.0448	-0.0550
β	0.340	0.090	-0.098
γ	2.016	0.000	-6.048

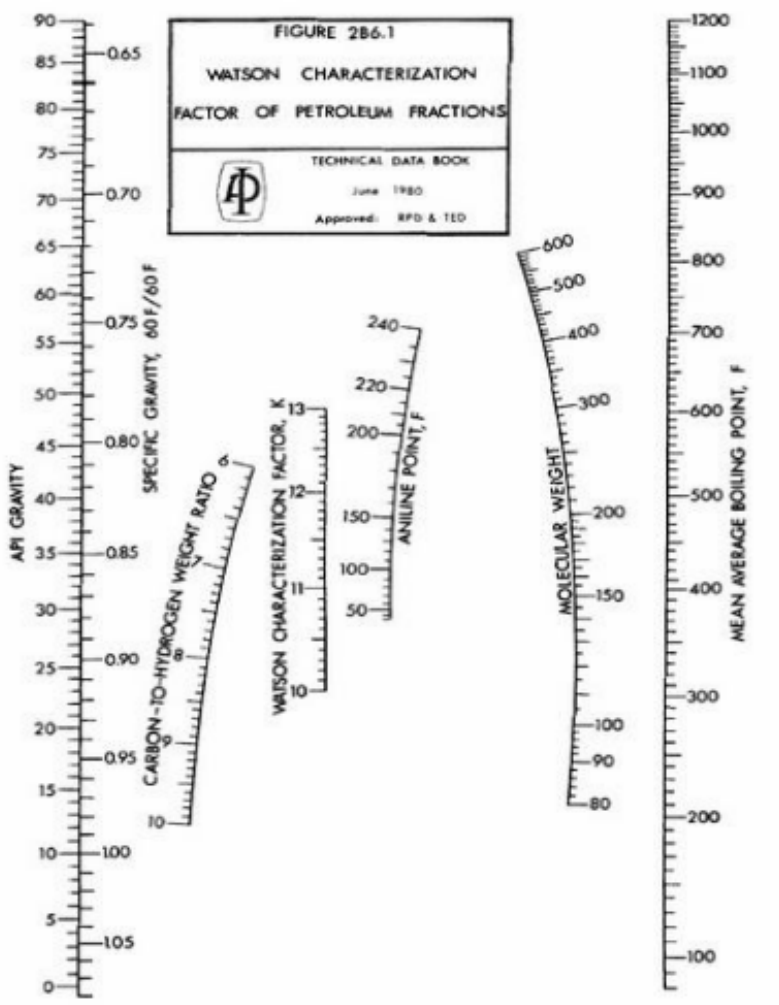
Appendix C

Nomograms

C.1 Viscosity Gravity Constant Nomogram - ASTM[3]



C.2 Winn Nomogram[13]



Appendix D

PNA Composition Based on Averaged Properties

With group-averaging method, the steps are as follows:

STEP 1: Find MW and liquid molar volume for every PNA compounds. Calculate specific volumes for the PNA families using Equation D.1, D.2 and D.3 respectively.

$$v_p = 14.026n - 14.026 \tag{D.1}$$

$$v_n = 16.280n + 31.102 \tag{D.2}$$

$$v_a = 149.34ln(n) - 213.43 \tag{D.3}$$

The molecular weights for paraffinic, naphthenic and aromatics are calculated using equations D.4, D.5 and D.6 respectively.

$$M_p = 14.026n + 2.016 \tag{D.4}$$

$$M_n = 14.026n - 14.016 \tag{D.5}$$

$$M_a = 11.792n + 2.258 \tag{D.6}$$

STEP 2: Solve the following simultaneous equations

$$\begin{bmatrix} 1 & 1 & 1 \\ v_p & v_n & v_a \\ M_p & M_n & M_a \end{bmatrix} \begin{bmatrix} x_p \\ x_n \\ x_a \end{bmatrix} = \begin{bmatrix} 1 \\ v \\ M \end{bmatrix}$$

The fraction molar volume should be calculated from MW and density of each fraction

STEP 3: change the molar composition to weight composition using Equation D.7

$$w_i = \frac{x_i \times M_n}{M_i} \tag{D.7}$$

Where i stand for p,n or A and M_n is molecular weight of SCN in question.

STEP 4: Apply Bergman corrections

$$0.03 \geq w_a \leq 0.35 \tag{D.8}$$

$$w_p \geq 0.2 \tag{D.9}$$

STEP 5: change weight compositions to molar compositions

$$x_i = \frac{w_i \times M_i}{M_n} \tag{D.10}$$

Due to incomplete availability of data, critical properties and acentric factor correlations for this method could not be developed.