CHARACTERIZATION OF WEST TEXAS INTERMEDIATE CRUDE OIL, AND
THE DEVELOPMENT OF TRUE BOILING POINT, DENSITY, AND VISCOSITY
CURVES FOR THE OIL WITH THE HELP OF ASTM STANDARD.

By

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Submitted In Partial Fulfillment of the Requirement for the Degree Of

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At

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DALHOUSIE UNIVERSITY
PETROLEUM ENGINEERING

The undersigned hereby certify that they have read and recommend to the Faculty of Graduate Studies for acceptance a thesis entitled “CHARACTERIZATION OF WEST TEXAS INTERMEDIATE CRUDE OIL, AND THE DEVELOPMENT OF TRUE BOILING POINT, DENSITY, AND VISCOSITY CURVES FOR THE OIL WITH THE HELP OF ASTM STANDARD.” by Prasad Subhash Mudgal in partial fulfilment of the requirements for the degree of Master of Engineering.

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<td>API</td>
<td>API gravity defined in equation (2.2)</td>
</tr>
<tr>
<td>A, B</td>
<td>Constants used in a distribution model developed by Riazi</td>
</tr>
<tr>
<td>a, b, ..., f</td>
<td>Correlation Constants in various equations</td>
</tr>
<tr>
<td>CH</td>
<td>Carbon- to- hydrogen weight ratio</td>
</tr>
<tr>
<td>l</td>
<td>Refractive Index parameter used in section 2.2.2.1</td>
</tr>
<tr>
<td>Kw</td>
<td>Watson characterization factor defined by equation (2.6)</td>
</tr>
<tr>
<td>ln, log</td>
<td>Natural Logarithm (base e), Logarithm to the base 10</td>
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<td>M</td>
<td>Molecular Weight, g/mol (kg/kmol)</td>
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<td>Pc</td>
<td>Critical pressure, bar</td>
</tr>
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<td>psat</td>
<td>Saturation pressure, bar</td>
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<tr>
<td>pvap</td>
<td>Vapor pressure, bar</td>
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<td>SG</td>
<td>Specific gravity at temperature of 15.5 °C (60°F) defined in equation (2.1)</td>
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<td>Tb</td>
<td>Boiling point, Kelvin</td>
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<tr>
<td>Tc</td>
<td>Critical Temperature, Kelvin</td>
</tr>
<tr>
<td>Tsat</td>
<td>Saturation Temperature, Kelvin</td>
</tr>
<tr>
<td>Vc</td>
<td>Critical molar volume, cm³/gmol</td>
</tr>
<tr>
<td>xi</td>
<td>Volume fraction, mole fraction, or weight fraction of a petroleum fraction</td>
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Greek Letters

ν - Kinematic viscosity, cSt (mm$^2$/s)
ω - Acentric factor defined in equation (2.3)
η - Refractive Index at 20°C.
ρ - Density at 15.5°C, kg/m$^3$
ρ$_{20}$ - Density at 20°C, kg/m$^3$
μ - Dynamic or absolute viscosity, mPa·s
θ - A property of petroleum fraction such as $M$, $T_b$, $SG$, $P_c$, $\rho_{20}$, ........

Superscript and Subscript

° - Property of n-alkanes used in Twu correlations
∞ - Value of a property at θ→∞
20 - Value of a property at 20°C
38 - Value of kinematic viscosity at 38°C
99 - Value of kinematic viscosity at 99°C
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ABSTRACT

Crude characterization is performed to obtain the Crude oil assay. This assay is a collection of chemical and physical properties, and yields of a particular crude oil. It provides the basis for the economic valuation of crude oil, engineering design, and refining processing. The present project work was focused on developing the different property curves for West Texas intermediate (WTI) crude oil and evaluating different prediction methods of properties such as molecular weight, density, and kinematic viscosity. ASTM 2892 standard was implemented for the distillation of this crude oil. Eleven different petroleum fractions were obtained upon distillation. The properties such as specific gravity and kinematic viscosity of these fractions were also measured using corresponding ASTM standards. The physical properties of all fractions were then used collectively to construct property curves such as true boiling point curve, density curve, and molecular weight curve. Riazi’s distribution model was then used to extrapolate these curves. Different mathematical correlations available in literature were used to predict Molecular weights and kinematic viscosities of all petroleum fractions. Goossens’ correlation appeared to yield appropriate estimation of molecular weights. From the comparison between experimental and predicted values of kinematic viscosities of all the fractions, it is found that the estimations obtained from Moharam and Twu correlations were in good agreement with experimental values for the light petroleum fractions, but these correlations failed in the prediction of the viscosities for heavy petroleum fractions.
1 INTRODUCTION

Petroleum is a non-renewable source of energy, which is globally in demand. The depletion of petroleum based fuels is in its peak at industries; heating processes, transportation sectors, and domains. Petroleum is a complex mixture of organic matters. The major constituent present in petroleum are hydrocarbons, which is usually compounded with minor constituents like oxygen, nitrogen, and sulfur. In general, the petroleum is found in the form of gases, liquids, semisolids, and solids (Riazi, Characterization and properties of petroleum fractions, 2005). The crude oil and its liquid petroleum fractions are the main concern in this project.

Initially the reservoir fluid is extracted from the earth crust, then at the production site the oil is processed to separate the water and gases. Later, they bring the oil at atmospheric pressure and temperature. The product obtained is called as crude oil which consists of hydrocarbons from light hydrocarbons to heavy hydrocarbons. The crude oil after field processing is sent to a refinery where it is processed and produce different useful petroleum products. A petroleum refinery is a combination of different unit operations such as distillation towers, separators, pumps, heat exchangers, etc. Before transferring any kind of crude oil to the refinery, the thermodynamic and physical properties of the crude oil and its petroleum fractions need to be known. Moreover, the prior knowledge of boiling point ranges of petroleum fractions or products is also required before starting with the process of the crude oil in the refinery. The procedure of generating the data for the crude oil at a laboratory scale is referred as characterization of petroleum fluids.

Crude oils or petroleum fractions are a complex mixture of compounds. Therefore, some physical properties are measurable for mixtures e.g. specific gravity at 15.5°C , but some
properties such as average boiling point, molecular weights, and compositions cannot be measured easily. Furthermore, there are some properties which are not viable to measure because of time constraints, and cost. These properties need to be predicted from the easily measured properties. Over the decades, chemical and petroleum engineers have developed a variety of simple methods and correlations to predict the properties of fractions from the easily measured properties. These correlations have developed in such way that it should require minimum input parameters, ease of use, and accuracy in the prediction of specific property (Fahim M A, 2010). Calculation of average boiling point, conversion of boiling point data from one type to another type, molecular weights, and composition of hydrocarbons (paraffins-naphthenes-aromatics) of the fractions are referred as the initial steps in characterization of petroleum fractions. The determination of other properties such as density at specific temperatures, refractive index, critical properties, viscosities, CH ratio, acentric factor, sulfur content, aniline point, flash point, etc. are also part of the characterization of petroleum fractions. With the help of characterization, one can not only estimate the parameters and properties of petroleum fractions, but also can determine the compositions of the fractions in order to ensure the quality of petroleum products (Riazi, Characterization and properties of petroleum fractions, 2005).

Generally, the characterization of crude oil is presented in terms of several narrow boiling cuts with known composition and characterization parameters such as boiling point, molecular weight, specific gravity, and kinematic viscosity. Each narrow boiling point is considered as a petroleum fraction. Therefore, the characterization of the crude oil depends up on the characterization of the petroleum fractions, which indirectly depends on the characterization of pure hydrocarbons and its properties. The accurate characterization of crude oil or its fraction is very important for a refinery especially during the design and operation of units. A small error in
the prediction of any property can make big changes in design and operation specifications of units, which in turn effects on the plant cost, production cost, plant life, desire product specifications, and finally on the profit. Therefore, the use of appropriate characterization method to predict accurate properties of petroleum fractions can save a large portion of the additional investment (Riazi, Characterization and properties of petroleum fractions, 2005).

West Texas Intermediate crude oil (WTI) is produced in Texas and southern Oklahoma of USA, which is one of the world’s market crude used as benchmark for pricing other US crudes. According to the data from the Environment Canada (Environment Canada, 1994), the API gravity of WTI is 40.8 °API and the specific gravity is 0.8212.

In this project work, West Texas Intermediate crude oil is characterized in order to develop different property curves for the oil and to evaluate the different prediction methods of properties of petroleum fractions.

1.1 Project Objectives:

The objectives of the project are:

1. Distill out various petroleum fractions from WTI crude using standard test method ASTM D2892.

2. Measure the bulk properties such as specific gravity and kinematic viscosity of all fractions using ASTM standards.

3. Develop the true boiling point curve, density curve, molecular weight curve, and kinematic viscosity curve for WTI crude oil.
4. Use various physical property prediction methods available in literature to estimate properties like density, molecular weight, kinematic viscosity.

5. Evaluate different prediction correlations by comparing the results obtained.

1.2 Overview of the Project Report:

This project report is divided into seven main sections including with Introduction. The remaining sections are as follows:

Section 2, General literature review provides understanding about different physical properties of a crude oil or a petroleum fraction. Then discusses about average boiling points, how to develop a complete true boiling point curve, and how to predict the properties such as density, molecular weight, and kinematic viscosity.

Section 3, Literature review for experimental methods provides quick view over different standard test methods available in order to develop the true boiling point curve for WTI crude oil. Then discusses about various standard test methods that required for the measurement of density or specific gravity, and kinematic viscosity at their respective reference temperature.

Section 4, Experimental systems and procedures, describes the experimental setup of different test methods used and their respective procedure. The test methods included in this section are ASTM D2892, ASTM D1298, ASTM D445, and ASTM D2893.

Section 5, Results and discussion provides detailed information about the results obtained from the experiments such as distillation of WTI crude oil, and the measurement of specific gravity and kinematic viscosity. Then discusses about different property curves developed and evaluation of various property correlations used.

Section 6, Conclusion provide a summary of the key finding observed during the development of different property curves and the evaluation of different prediction correlations

Section 7, Suggestion for Future work provides a brief overview about the improvements and modifications that could be performed to this project work.
1.3 Roadmap of Project Work

West Texas Intermediate Crude Oil

Measurement of Basic Properties of WTI Crude Oil

Distillation of WTI Crude Oil Using ASTM D2892

Measurement of Properties of the Petroleum Fractions Using Respective ASTM Standards

Prediction of Density at 20°C, Molecular Weight, and Kinematic Viscosity using Basic

Development of TBP, Density, and Molecular Weight Curves

Comparison between Various Prediction Correlations used and Selection of More Accurate Correlation for the Properties.

WTI Crude Oil Assay
2 GENERAL LITERATURE REVIEW

2.1 Different Physical Properties and Parameters

Molecular weight ($M$)

Molecular weight of a hydrocarbon compound is the summation of atomic weights of different elements contains in the compound. It is normally applied to convert molar quantities to mass basis for practical applications. Also, it is one of the important characterization properties for pure hydrocarbons and petroleum fractions. Generally, the hydrocarbon compound includes elements are Carbon(C), Hydrogen(H), Sulfur(S), Oxygen(O), and Nitrogen(N) (Riazi, Characterization and properties of petroleum fractions, 2005). The atomic weights of these elements are $C = 12.011$, $H = 1.008$, $S = 32.065$, $O = 16.0$, $N = 14.01$, as specified in IUPAC standards (IUPAC, the International Union of Pure and Applied Chemistry., May 2013.). For example, the molecular weight of Cyclopentane ($C_5H_{10}$) is calculated as $12.011 \times 5 + 1.008 \times 10 = 70.1$ kg/kmol. The molecular weight is the indication of molecular structure and the size of that compound. The areas where the molecular weight plays a vital role are material or energy balance, thermodynamic phase equilibrium, reaction kinetics, unit operations such as distillation, extraction, and absorption, (Schneider , 1998). The molecular weight generally expressed in kg/kmol, g/mol or lb/mol.

Boiling point ($T_b$)

Boiling point of a petroleum fraction is the temperature at which it starts boiling and transfers from liquid state to vapor state at a pressure of 1 atm (Erling & Wei, 2005). In other words, it is the temperature at which the vapor pressure is equal to atmospheric pressure for the petroleum
fraction. At pressure of 1 atm, the boiling point is called normal boiling point which is indicated
by letters $T_b$. When the boiling point is at other pressures such as 1, 10, or 50 mm of Hg, then it
is termed as saturation temperature instead of normal boiling point (Riazi, Characterization and
properties of petroleum fractions, 2005). Boiling point is one of the essential characteristic
parameters generally used to determine the volatility of different petroleum fractions and to
predict the physical properties of the fractions such as molecular weight ($M$), viscosity ($\mu$),
composition of hydrocarbons ($x_i$), acentric factor ($\omega$), critical properties ($T_c$, $P_c$, and $V_c$),
refractive index ($\eta$), etc.

Density ($\rho$), Specific Gravity ($SG$) and API Gravity

Density of any liquid is the mass per unit volume. It is a temperature and pressure dependent
property, where the density of a liquid decreases as the temperature increases, and vice versa. In
general, the pressure affects the density of liquid, but the change is not as profound as
temperature. The units used to express the density are kg/m$^3$, g/cm$^3$ and lb/ft$^3$. The density
frequently expressed at reference condition of 20°C and 1 atm for petroleum fractions (Daubert T E, 1997).

Specific gravity ($SG$) is also called relative density which is defined as density of a liquid divided
by density of water at the same conditions of temperature and pressure. The standard conditions
at which the specific gravity is expressed are 15.5°C(60°F) and 1 atm (Daubert T E, 1997). The
specific gravity at 15.5°C is usually employed as an input parameter along with boiling point ($T_b$)
to predict the different physical properties of petroleum fractions. Mathematically it can be
defined as

$$\text{Specific gravity, 60F/60F} = \frac{\text{density of liquid at 60°F}}{\text{density of water at 60°F}} \quad (2.1)$$
In petroleum industry, API gravity is widely used to qualify the petroleum fractions which was introduced by the American Petroleum Institute (API). The API gravity is defined as

\[
\text{API gravity} = \frac{141.5}{SG(\text{at}60/60^\circ F)} - 131.5
\]  

Generally, API gravity values are higher for light hydrocarbon fractions and lower for heavy hydrocarbon fractions. Sometimes, it has been used as an input parameter with Watson characterization factor \((K_w)\) to predict the properties such as molecular weights and kinematic viscosities of the fractions. It is usually expressed in the unit of degree API (Riazi, Characterization and properties of petroleum fractions, 2005).

Critical Properties \((T_c, P_c, V_c)\)

In Temperature-Pressure-Volume diagram, the critical point is a state of phase at which both liquid and vapor phase can co-exist at equilibrium. It is the point at which all intensive properties of liquid phase and vapor phase are equal. The corresponding temperature, pressure, and volume at the critical point are called critical temperature \((T_c)\), critical pressure \((P_c)\), and critical volume \((V_c)\) respectively. Any gas above its critical temperature cannot be liquefied with mere change of pressure. Also a liquid above its critical pressure cannot be converted to gas phase no matter how much is the temperature. Any fluid above its critical point condition is called supercritical fluid. The critical volume \((V_c)\) is the molar volume at its critical temperature and pressure \((T_c\) and \(P_c)\) (Riazi, Characterization and properties of petroleum fractions, 2005).

The critical properties of hydrocarbon or petroleum fractions are very important for determination of existing phase conditions, allowable operating ranges of reactors and mass-transfer equipment such as distillation towers, absorbers, stripping columns, etc. (Daubert T E,
These properties are also used to calculate thermodynamic, physical, and transport properties of the petroleum fractions.

Acentric Factor ($\omega$)

Acentric factor is one of the characterization parameters developed by Pitzer, to improve the accuracy of the corresponding equations of state for heavy hydrocarbons. It is defined as a measure of deviation in the thermodynamic properties of a particular fluid to those properties calculated from the principle of corresponding states. The following equation is used for calculation of acentric factor ($\omega$) (Riazi, Characterization and properties of petroleum fractions, 2005).

$$\omega = - \log_{10}(P_r^{\text{vap}}) - 1.000$$

(2.3)

where, $P_r^{\text{vap}}$ is a reduced vapor pressure, $P_v^{\text{ap}}/P_c$, and it is a dimensionless parameter. $P_v^{\text{ap}}$ is the vapor pressure at $T=0.7\times T_c$, in bar. $P_c$ is the critical pressure, in bar. $T_c$ is the critical Temperature, in K. $T$ is the temperature, in K.

In other words, it is a measure of deviation in the thermodynamic properties of a particular fluid to the properties of ideal spherical molecules (e.g. noble gases such as helium, argon, xenon, etc.). For noble gases $\omega=0$, as hydrocarbon molecules are non-spherical, they have an acentric factor not equal to zero and it increases with an increase in the molecular weight of the fraction (Erling & Wei, 2005). Indirectly it serves as an estimation of the size and shape of molecules comprised in the petroleum fractions (Daubert T E, 1997).
Refractive Index \((n)\) –

Refractive index is the ratio of velocity of light in a vacuum to the velocity of light in a fluid for which refractive index is to be measured. Refractive index is a dimensionless quantity and a state function, which depends on the temperature and pressure of the fluid.

\[
n = \frac{\text{velocity of light in the vacuum}}{\text{velocity of light in the fluid}} \quad (2.4)
\]

The velocity of light is different for different mediums. The vacuum and gases have the velocity of light at maximum level, while it is somewhat less for liquids. Therefore, refractive index \((n)\) is more than unity for the liquid medium, whereas it is close to unity for gaseous medium. Refractive index is an important characterization parameter usually used to recognize the molecular type composition. For example, \(n = 1.3326\) for n-butane (paraffin), \(n = 1.4503\) for n-undecylcyclopentane (naphthane), and \(n = 1.4972\) for m-xylene (aromatic). The refractive index values increases from paraffin to aromatic hydrocarbons (Riazi, Characterization and properties of petroleum fractions, 2005).

Vapor Pressure \((P^{\text{vap}})\)

At thermodynamic equilibrium state, the vapor pressure of a particular substance is the force exerted per unit area by the vapors of liquid or solid present in a system. In other words, it is the pressure at which the vapor phase of a substance is equilibrium with the liquid or solid phase of the substance. The vapor pressure is also called as saturation pressure \((P^{\text{sat}})\) and the corresponding temperature is termed as saturation temperature \((T^{\text{sat}})\) (Daubert T E, 1997).

The vapor pressure increases non-linearly with temperature. Below atmospheric pressure, the vapor pressure of a liquid at any temperature is always less than 1 atm. As the vapor pressure
approaches to atmospheric pressure, the saturation temperature also moves towards to the boiling point temperature. As mentioned earlier, the boiling point is the temperature at which the vapor pressure of a substance is equal to the atmospheric pressure. The highest vapor pressure of any substance is the critical pressure of that substance. Vapor pressure is the property that indicates the volatility of a liquid. It is usually used in the calculation physical properties, vapor loss and flammability range of a liquid. As higher the vapor pressure of a liquid, more volatile the liquid is. More volatile liquids usually have higher critical pressure, lower critical temperature, lower density, and lower boiling point (Riazi, Characterization and properties of petroleum fractions, 2005).

Dynamic viscosity ($\mu$) and Kinematic viscosity ($\nu$)

When a fluid is flowing, the dynamic viscosity ($\mu$), is the ratio of the shear stress ($\tau$) in the flow to the shear rate of deformation ($\partial u / \partial y$) in the fluid. Dynamic viscosity is nothing but the measure of resistance to flow of the fluid. It is depends upon the type of fluid, time required for flowing the fluid, temperature and pressure of the environment in which the fluid is flowing. The dynamic viscosity is expressed in Pascal-second (Pa·s) or poise (P).

Kinematic viscosity ($\nu$) is the ratio of the dynamic viscosity ($\mu$) of a fluid to the density ($\rho$) of that fluid at the same temperature.

$$\nu = \frac{\mu}{\rho}$$  \hspace{1cm} (2.5)

Kinematic Viscosity is the ratio of momentum transfer to momentum storage. These kinds of ratios are called diffusivities, which has unit of meter square per second (m$^2$/s) or cSt (mm$^2$/s) (ASTM 445, 1998). Dynamic and kinematic viscosities are transport properties used for
characterization of hydrocarbons. Many petroleum products are used as lubricants in machines or equipment. The good functioning of machines or equipment depends upon the viscosity of the lubricants that have been used. The dynamic viscosity as well as the kinematic viscosity both are used to predict the physical properties, develop the process design, design the equipment, storage and transport facilities.

Watson Characterization Factor \((K_w)\)

In 1933, Watson and Nelson proposed the characterization parameter. Watson characterization factor \((K_w)\) correlates two physical properties namely average boiling point and specific gravity. The factor is defined as (Riazi, Characterization and properties of petroleum fractions, 2005)

\[
K_w = \frac{(1.8 \times T_b)^{1/3}}{SG} \tag{2.6}
\]

Where, \(T_b\) is the average boiling point, in \(K\); \(SG\) is the specific gravity at 60°F (15.2°C). The Watson characterization factor helps to determine the different molecular compositions such as paraffinic, naphthenic, and aromatic in the hydrocarbon fractions. It shows the compositions in a specific range of 13.0 (high paraffinic) to 10.0 (highly aromatic) (Whitson, 1983). By using Riazi and Daubert relation for molecular weight, Whitson developed a new correlation based on the molecular weight and specific gravity of hydrocarbons is followed as

\[
K_w = 4.5579M^{0.15178}SG^{-0.84573} \tag{2.7}
\]

The Watson characterization factor is also used in predicting different physical properties of petroleum fractions such as kinematic viscosity, API gravity, molecular weight, etc.
Flash Point

Flash point is the lowest temperature at which vapor pressure of a petroleum fraction can produce sufficient vapors to form ignitable mixture in the surrounding air. To ignite the mixture an external source is required as spark or flame. The hydrocarbons with high vapor pressures (light hydrocarbons) have low flash points and vice versa. Flash points of hydrocarbons are directly proportional to its boiling points. Flash point is a very essential parameter for safety circumstances, such as storage of hydrocarbons or transportation of hydrocarbons. The flash point of any hydrocarbon fraction should be more that of surrounding temperature to minimize the possibility of fire (Riazi, Characterization and properties of petroleum fractions, 2005).

Aniline Point

Aniline point is the lowest temperature at which a petroleum fraction is miscible with the same volume of aniline. It is the parameter used to estimate share of aromatics in the petroleum fractions. Aniline point of a hydrocarbon depends upon the molecular weight and carbon number of that hydrocarbon. It increases as the molecular weight and the carbon number increases (Daubert T E, 1997). Heavy hydrocarbons have low aniline points because aniline itself is an aromatic compound; heavy hydrocarbons are easily miscible with aniline as compared to light hydrocarbons. ASTM procedure D611 is used to determine aniline points experimentally (Riazi, Characterization and properties of petroleum fractions, 2005).
Cloud point, Freezing Point and Melting point

Sometimes, the heavy hydrocarbons, especially waxes, tar, and asphalt, lose their fluidity and turn into solid. This solidification causes some serious problems in process, storage and transportation of hydrocarbons. Therefore, by considering safety the knowledge of cloud point, freezing point and melting point is substantive. The cloud point is the lowest temperature at which wax crystals begin to form crystals in heavy hydrocarbon fractions by a gradual cooling under standard condition. The freezing point is the temperature at which pure hydrocarbons solidify at 1 atm. The melting point is the temperature at which pure hydrocarbons start to liquefy or melt at 1 atm (Riazi, Characterization and properties of petroleum fractions, 2005).
2.2 Characterization of Petroleum Fractions

2.2.1 Development of TBP curve

There are various standard distillation methods such as ASTM D86, ASTM D2892, ASTM D2887 (simulated distillation), and equilibrium flash vaporization through which the boiling point curve can be obtained. The curves obtained from above distillation methods are different from each other. The most useful and reliable curve is true boiling curve (TBP) which indicates appropriate separation of petroleum fractions or products. The boiling point curve from ASTM D2892 is the true boiling curve, because ASTM D2892 uses 15 theoretical plates column to achieve a high degree of separation. Whereas the curves obtained from the other methods ASTM D86, ASTM D2887, and equilibrium flash vaporization are not in the form of TBP curve; the boiling points from these methods will not indicate true boiling points for petroleum fractions. Therefore, these curves are need to be converted into the form of TBP curves. While there is no conversion needed for ASTM D2892’s TBP curve; it can be used directly for further use such as characterization procedure, physical property predictions, or design and control of distillation column. In following sections, the concept of average boiling points and the prediction of complete distillation curve are discussed.

2.2.1.1 Average Boiling Points

The boiling points for crude oils or petroleum fractions are represented by the distillation curves or TBP curves. But for the prediction of physical properties or characterization of a hydrocarbon fraction, a single value of boiling point is required. Therefore, an average or a middle point of a boiling point range of a particular fraction is used as the single characterizing boiling point for that fraction. There are five different types of average boiling points which are normally used in characterization. The first three are VABP (volume average boiling point), MABP (molal
average boiling point), and WABP (weight average boiling point). These average boiling points are defined by following equations (Riazi, Characterization and properties of petroleum fractions, 2005).

Volume Average Boiling Point

\[ VABP = \sum_{i=1}^{n} x_v T_{bi} \] (2.8)

Molal Average Boiling Point

\[ MABP = \sum_{i=1}^{n} x_i T_{bi} \] (2.9)

Weight Average Boiling Point

\[ WABP = \sum_{i=1}^{n} x_w T_{bi} \] (2.10)

where \( x_v \), \( x_i \), and \( x_w \) are the volume fraction, mole fraction, and weight fraction of the component \( i \) respectively. \( T_{bi} \) is the normal boiling point of component \( i \) in Kelvin. The remaining two average boiling points are CABP (cubic average boiling point) and MeABP (mean average boiling point). These boiling points are defined by following equations (Riazi, Characterization and properties of petroleum fractions, 2005).

Cubic Average Boiling Point is calculated by using following equation

\[ CABP = \left( \frac{1}{1.8} \right) \left[ \sum_{i=0}^{n} x_{vi} \left( 1.8T_b - 459.67 \right)^{1/3} \right]^{3} + 255.37 \] (2.11)
Mean Average Boiling Point

Mean average boiling point is the arithmetic average of the molal average boiling point (MABP) and cubic average boiling point (CABP).

\[ MeABP = \frac{MABP + CABP}{2} \]  

(2.12)

Where, \( T_{bi} \) is the normal boiling point of component \( i \) in Kelvin.

For petroleum fractions whose volume, mole, or weight fractions are not known, then the average boiling point can be calculated as

\[ ABP = \frac{\text{initial boiling point of a fraction} + \text{final boiling point of that fraction}}{2} \]  

(2.13)

The average boiling point is the most important parameter in predicting various physical properties of a petroleum fraction such as molecular weight, density, specific gravity, kinematic viscosities, API gravity, Watson factor, etc.

2.2.1.2 Complete True Boiling Point Curve

Generally, TBP curve data rarely available for entire range of percent distilled. In many cases, the data is obtained up to 60, 65, or 70% distilled point for any petroleum fractions or crude oils. The reason behind this, the petroleum fractions or crude oils contain heavy hydrocarbons towards the end of the curve. The more heavy hydrocarbons are in a fraction or crude oil, the more difficult is to achieve accurate boiling points for that fraction or crude oil. Sometimes, the TBP data is available only up to 50% distilled point and it is because of more heavy hydrocarbons in the sample. But the curve up to 90 - 95% distilled point is critically important for process engineers, characterization, and design of distillation columns. Therefore, the
fractions or crude oils whose curves end at 50, 60, or 70% point, these curves need to be extended up to 90 or 95% point by using available data.

There is a model namely “Distribution Model” which is developed by Riazi, this model is based on a probability distribution model for properties of heptanes-plus fractions. This model can be used to complete the TBP curves up to 95% point. The model is defined by the following equation (Riazi, Distribution Model for Properties of Hydrocarbon-Plus Fractions, 1989):

\[
\frac{T - T_0}{T_0} = \left[ \frac{A}{B} \ln \left( \frac{1}{1 - x} \right) \right]^{1/B}
\]

(2.14)

where, \( T \) is the temperature on the boiling points curve. \( x \) is the volume or weight fraction of the sample distilled. \( A, B, \) and \( T_0 \) are the three parameters need to be evaluated on the available data of boiling points through a linear progression. Actually, \( T_0 \) is the initial boiling point (\( T \) at \( x=0 \)) but has to estimate from actual data with \( x > 0 \). By selecting a value of \( T_0 \), which must be lower than the first value of \( T \) in the data set. (Riazi, Characterization and properties of petroleum fractions, 2005). The model can be solved to predict complete TBP curve using a linear regression or Solver (in Tools) in Excel spreadsheets. The solving procedure is pretty straightforward. \( A, B, \) and \( T_0 \) are the three parameters need to be evaluated by putting the model in the linear regression form \( Y = C_1 + C_2 X \) where \( Y = \ln \left( \frac{T - T_0}{T_0} \right) \) and \( X = \ln \ln \left( \frac{1}{1 - x} \right) \). Once the appropriate parameter is achieved, the further boiling points on the TBP curve up to desired point can be estimated (Riazi, Distribution Model for Properties of Hydrocarbon-Plus Fractions, 1989).
2.2.2 Prediction of Hydrocarbon Properties

2.2.2.1 Prediction of Density

The density (ρ) and specific gravity (SG) of petroleum fractions are bulk properties which can be directly measured with high accuracy. The density at reference temperature of 20°C and 1 atmospheric pressure is one of the major parameters used in the characterization of petroleum fractions. If the specific gravity at 15.5°C is available then with rule of thumb, $\rho_{20} = 0.995$ SG is the simplest form to determine density at reference temperature of 20°C (Riazi, Characterization and properties of petroleum fractions, 2005).

There is another equation for predicting the density at 20°C; the equation uses the specific gravity at 15.5°C for calculating the density. The equation is more accurate for petroleum fractions with narrow boiling point ranges. The equation is as follows (Riazi, Characterization and properties of petroleum fractions, 2005)

$$\rho_{20} = SG - 4.5 \times 10^{-3}(2.34 - 1.9SG)$$  \hspace{1cm} (2.15)

If the density at 20°C is already known, then the above equation can also be implemented in reverse manner in order to calculate the specific gravity at 15.5°C. The above equation become as follows (Riazi, Characterization and properties of petroleum fractions, 2005)

$$SG = 0.9915\rho_{20} + 0.01044$$  \hspace{1cm} (2.16)

Riazi and Daubert (1987), constructed a simple equation that is “Two-parameter equation” for predicting the properties of undefined petroleum fractions. The equation is given as

$$\theta = a\theta_1^b \theta_2^c$$  \hspace{1cm} (2.17)
where, $\theta$ is the property to be predicted. $\theta_1$ and $\theta_2$ are any two input parameters that should represent molecular energy and molecule size. This input parameters pair ($\theta_1$, $\theta_2$) can be ($T_b$, $SG$), ($T_b$, $I$), ($T_b$, $CH$), ($M$, $SG$), ($M$, $I$), ($M$, $CH$), ($\mu$, $SG$), ($\mu$, $I$), or ($\mu$, $CH$) where, $T_b$ is normal boiling point, in Kelvin. $I$ is the refractive index parameter at 20°C. $M$ is molecular weight. $CH$ is Carbon to Hydrogen weight ratio. $SG$ is the specific gravity at 15.5°C, and $\mu$ is the kinematic viscosity at 38°C. The constants $a$, $b$, and $c$ are based on the properties of hydrocarbons with carbon number range $C_5$ to $C_{20}$. This range is equivalent to the molecular weight range of 70-300, and the boiling point range from 300 to 616 K (26 to 343.33 °C). By using this equation, properties such as density at 20°C, molecular weight, critical properties, refractive index, and heat of vaporization can be predicted successfully (Riazi & Daubert, Characterization Parameters for Petroleum Fractions, 1987). For predicting the density at 20°C, the following equation is developed by putting appropriate values of constants in the two-parameter equation (Riazi & Daubert, Characterization Parameters for Petroleum Fractions, 1987):

\[
\text{for } M \leq 300 \quad \rho_{20} = 0.9837T_b^{0.002}S_G^{1.005} \tag{2.18}
\]

Riazi and Roomi (2001) studied about the applications of refractive index, $n$ in the estimation of properties of hydrocarbon fractions, and they developed another equation by using two-parameter equation for predicting the density at 20°C. The equation is valid for heavy petroleum fractions with molecular weight $M \geq 300$ [31]. The equation is given as

\[
\text{for } M \geq 300 \quad \rho_{20} = 2.8309M^{0.04}I_{20}^{1.1354} \tag{2.19}
\]

where, $M$ is the molecular weight, $I = (n^2 - 1/n^2 + 2)$ is the refractive index parameter. $I_{20}$ is the parameter calculated from refractive index, $n$ which is measured at 20°C.
2.2.2.2 Prediction of Molecular Weight

Molecular weight, is one of the important physical characteristic for petroleum fractions in petroleum industry. The experimental determinations of molecular weights of the fractions are difficult, but still the accurate determination or prediction of molecular weight is crucial for analysis of hydrocarbon processing. The molecular weights not only help in predicting other physical properties of the fractions, but also plays an important role in thermodynamic phase equilibrium, reaction kinetics, and vapor density calculations of hydrocarbons.

There are various mathematical correlations that have been developed to predict the molecular weights of hydrocarbons. Most of these correlations are based on the basic properties of average boiling points and specific gravities. All of these correlations are applicable when an experimental data is not available for hydrocarbons or undefined petroleum fractions. Some of the prediction correlations are discussed further in this section.

Riazi and Al-Sahhaf (1995), proposed a general equation to predict the different properties of hydrocarbons by using molecular weight as a basis for that equation. The equation is proposed as

\[ \ln(\theta_\infty - \theta) = a - b M^c \]  

(2.20)

where, \( M \) is the molecular weight of hydrocarbon. \( \theta \) can be any property to be estimated. The constants \( a, b, c, \) and \( \theta_\infty \) for n-alkanes, n-alkylcyclopentanes, n-alkylcyclohexanes, and n-alkylbenzenes which are given in the same proposal (Riazi & Al-Sahhaf, Physical Properties of n-Alkanes and n-Alkylhydrocarbons: Application to Petroleum Mixtures, 1995). If \( \theta \) is considered as normal boiling point for hydrocarbon and the value of boiling point for given hydrocarbon is known, then the above equation can be used in reverse direction in order to calculate the molecular weight of that hydrocarbon. The above equation can be written in the
form of normal boiling point ($T_b$) as (Riazi, Characterization and properties of petroleum fractions, 2005)

$$M = \left\{ \frac{1}{b} [a - \ln(T_\infty - T_b)] \right\}^{1/c} \quad (2.21)$$

where, $M$ is the molecular weight of hydrocarbon to be determined. $T_b$ is the known normal boiling point for that hydrocarbon, in Kelvin. The above proposed equation is only valid for pure hydrocarbons of different homologous groups.

As discussed in previous section 2.2.2.1, the two-parameter equation developed by Riazi and Daubert [30] can be used to determine molecular weight of hydrocarbons or undefined petroleum fractions. The two-parameter equation in order to predict molecular weight has become (Riazi, Characterization and properties of petroleum fractions, 2005).

$$M = 1.6607 \times 10^{-4} T_b^{2.1962} S G^{-1.0164} \quad (2.22)$$

As mentioned earlier, this equation (two-parameter equation) gives accurate molecular weights up to 300 for hydrocarbons, above this limit it fails to predict proper molecular weights. According to Tsonopoulos et al., (1986) the equation (2.22) works properly for coal liquid fractions. Therefore, they recommended the equation for prediction of molecular weight of coal liquid fractions.

In order to increase the application range of two-parameter equation, Riazi and Daubert (1987) modified two-parameter equation and its constants. Then they developed a new equation with more accuracy. The modified equation is given as

$$\theta = a \exp[b \theta_1 + c \theta_2 + d \theta_1 \theta_2] \theta_1^e \theta_2^f \quad (2.23)$$
where, \( a-f \) are the modified constants for various parameters of \( \theta \) and pairs of \((\theta_1, \theta_2)\) given in the proposal (30). Once the constants for molecular weights are placed in the modified equation, the equation is turned into the following form (Riazi, Characterization and properties of petroleum fractions, 2005).

\[
M = 42.965[\exp(2.097 \times 10^{-4}T_b - 7.78712 SG + 2.08476 \times 10^{-3}T_bSG)]T_b^{1.26007}SG^{4.98308}
\]

(2.24)

The equation is valid for the hydrocarbons with molecular weight range from 70 to 700, and boiling point range from 300 to 850 K (32 to 566°C), which is equivalent to the API range from 14.4 to 93.1 (Daubert T E, 1997). This equation has been included in API-TDB Petroleum Refining (Daubert T E, 1997) as one of the prediction methods for molecular weights of petroleum fraction. Equation (2.24) gives accurate molecular weight predictions for light hydrocarbons with an error of 3.4%, while for heavy hydrocarbons with the error of 4.7% (Daubert T E, 1997).

In 1976, Kesler and Lee proposed a new correlation for prediction of molecular weight on the basis of regression analysis of hydrocarbon data within molecular range of 60 to 650. The proposed correlation is written as (Riazi, Characterization and properties of petroleum fractions, 2005)

\[
M = \frac{-12272.6 + 9486.4SG + (8.3741 - 5.9917SG)T_b + (1 - 0.77084SG - 0.02058SG^2) \times (0.7465 - 222.466/T_b) 10^7/T_b + (1 - 0.80882SG + 0.02226SG^2) \times (0.3228 - 17.335/T_b) 10^{12}/T_b^3}{T_b^{1.26}SG^{4.98}
\]

(2.25)

The use of Equation (2.25) is recommended up to a boiling point of approximately 750 K (~890°F).
The work of Twu (1984) proposed a set of dependent correlations to predict molecular weights of undefined petroleum fractions. In the theoretical approach, Twu firstly correlated the critical temperature ($T_c^o$), molecular weight ($M^o$), and specific gravity ($SG^o$) of $n$-alkanes with the boiling point ($T_b$). Then the difference between the specific gravity of the undefined fraction ($SG$) and the specific gravity of n-alkane ($SG^o$) was used in conjunction with the molecular weight of n-alkane in order to predict the molecular weight of the fraction ($M$) (Riazi, Characterization and properties of petroleum fractions, 2005). In other words, the molecular weights of the fractions were predicted based on their deviations from the molecular weights of $n$-alkanes (Schneider, 1998). The Twu correlations are given as follows (Hassan, 2010)

$$\beta = \ln M^o$$  \hspace{1cm} (2.26)

$$k = \exp(5.12640 + 2.71579\beta - 0.286590\beta^2 - 39.8544/\beta - 0.122488/\beta^2) - 13.7512\beta + 19.6197\beta^2$$  \hspace{1cm} (2.27)

$$T_c^o = k (0.533272 + 0.34383 \times 10^{-3}k + 2.52617 \times 10^{-7}k^2 - 1.658481 \times 10^{-10}k^3 + 4.60773 \times 10^{24}k^{-13})^{-1}$$  \hspace{1cm} (2.28)

$$\alpha = 1 - (k/T_c^o)$$  \hspace{1cm} (2.29)

$$SG^o = 0.843593 - 0.128624\alpha - 3.3615\alpha^3 - 13749.5\alpha^{12}$$  \hspace{1cm} (2.30)

$$\Delta SG_M = \exp[5(SG - SG^o)] - 1$$  \hspace{1cm} (2.31)

$$x = |0.012342 - 0.244541/k^{0.5}|$$  \hspace{1cm} (2.32)

$$f_M = \Delta SG_M[x + (-0.0175691 + 0.143979/k^{0.5})\Delta SG_M]$$  \hspace{1cm} (2.33)

$$\ln(M) = (\ln M^o)[(1 + 2f_M)/(1 - 2f_M)]^2$$  \hspace{1cm} (2.34)

where, $k = T_b/1.8$, it is used to convert the unit of true boiling point ($T_b$) from Rankin to Kelvin. $T_b$ is the boiling point of the fraction, and $M$ is the molecular weight of the fraction is to be
determined. The proposed set of equations is not specific in calculating the molecular weight of n-alkane ($M^o$); an iterative process required to obtain the molecular weight ($M^o$) (Riazi, Characterization and properties of petroleum fractions, 2005).

Recently, Goossens (1996) developed a simple prediction method for molecular weights of petroleum fractions with the full practical range of 75-1700. The correlation was developed on the data that collected from the study of 40 pure hydrocarbons and 23 different petroleum fractions. The equation is based on the two parameters, the normal boiling point ($T_b$) and the density at 20°C ($\rho_{20}$) of a petroleum fraction. The correlation is proposed as follows

$$M = 0.010770T_{b}^{1.52869+0.06486ln(T_{b}/(1078-T_{b}))}/\rho_{20}$$ (2.35)

Equation (2.35) is applicable for the carbon range of C₅-C₁₂₀, which is equivalent to the boiling point range of 300-1000 K and the density range of 0.63-1.08. There were around 63 data points used to obtain the constants in equation (2.35); the equation predicts the molecular weights of the fractions with an error of only 2% (Goossens, 1996)

During the period before 1950s, there were no computational methods available. At that time there was a trend to develop correlations with the help of graphical methods. The graphical representation of equations is nothing but a nomogram or nomograph, where different input parameters are graphically correlated with the desired property. It is usually designed when more than two properties are involved.

If any two values of input parameters are available, then the desired property estimation can be made by drawing a straight line through these points and extending the line until it cuts to the desired property line. In 1957, Winn developed a nomogram for different properties of petroleum
fractions. The properties included in the nomogram are API gravity, specific gravity (SG), carbon to hydrogen weight ratio (CH), Watson characterization factor ($K_w$), aniline point, molecular weight ($M$), and mean average boiling point ($T_b$). The nomogram developed by Winn is shown in figure 2.1. It can be observed that the nomogram is designed such that the most suitable input parameters ($T_b$) and (SG) are placed opposite to each other; so that the range of applicability can be wider. In petroleum industry, the use of nomogram is still exists, it can be used for an instant prediction of properties or quick analysis of calculations made from theoretical correlation (Riazi, Characterization and properties of petroleum fractions, 2005).

*Figure 2.1 Winn nomogram for characterization of petroleum fractions. (Daubert T E, 1997)*
2.2.2.3 Prediction of Kinematic viscosity

The definition of dynamic viscosity (μ) and kinematic viscosity (ν) are already mentioned in section 2.1. As mentioned earlier, the both properties are transport properties of petroleum fractions; especially the kinematic viscosity (ν) plays very important role in the characterization of petroleum fractions as well as in the petroleum processing industry. The kinematic viscosity normally measured at the reference temperature of 38 °C (100°F) and 99 °C (210°F) (Daubert T E, 1997). The viscosities at these respective temperatures ν₃₈ and ν₉₉ are generally considered as basic characterization parameters.

The prediction of kinematic viscosities of fractions is more complicated as compared to other physical properties predictions. Specifically, for heavy petroleum fractions the accurate predictions are rarely observed. However, there are some prediction methods developed in order to predict the kinematic viscosities when experimental data is unavailable. Most of the prediction methods are based on the parameters of $T_b$, SG, API gravity and Watson factor ($K_w$).

The API-TDB (Daubert T E, 1997) included a method for the prediction of kinematic viscosities of undefined petroleum fractions; the method is developed by Fitzgerald. The purpose of this method is to predict the viscosities of petroleum fraction at any temperature at low pressure. However, the method can be used to predict the viscosities at near to atmospheric pressure. The method has several equations which are given as

At 38°C (100°F),

$$\nu_{38} = \nu_{ref} + \nu_{cor}$$  \hspace{1cm} (2.36)

$$\log \nu_{ref} = -1.35579 + 8.16059 \times 10^{-4}T_b + 8.38505 \times 10^{-7}T_b^2$$  \hspace{1cm} (2.37)
\[ \log \nu_{cor} = A_1 + A_2 K \]  

(2.38)

where,

\[ A_1 = c_1 + c_2 T_b + c_3 T_b^2 + c_4 T_b^3 \]  

(2.39)

\[ A_2 = d_1 + d_2 T_b + d_3 T_b^2 + d_4 T_b^3 \]  

(2.40)

\[ c_1 = 3.49310 \times 10^1 \]

\[ d_1 = -2.92649 \]

\[ c_2 = -8.84387 \times 10^{-2} \]

\[ d_2 = 6.98405 \times 10^{-3} \]

\[ c_3 = 6.73513 \times 10^{-5} \]

\[ d_3 = -5.09947 \times 10^{-6} \]

\[ c_4 = -1.01394 \times 10^{-8} \]

\[ d_4 = 7.49378 \times 10^{-10} \]

\( T_b \) is the mean average boiling point, in degree Rankin, \( \nu_{38} \) is the kinematic viscosity at 38°C, in cSt, and \( SG \) is the specific gravity at 60 F/60 F.

At the time of testing, there were 7000 data points taken into consideration and the results were obtained with overall error of 14%. Actually, the error was somewhat low for light hydrocarbons then heavy hydrocarbons; for API greater than 30 the error observed was 8%. The method is applicable for boiling point range of 339-922 K (Daubert T E, 1997).

Abbott et al (1971) developed a correlation in order to determine the kinematic viscosities of petroleum fractions. The method is used Watson characterization factor \( (K_w) \) and API gravity as input parameters. In addition, they have presented this method in the form of nomogram. The proposed equation is written as (Riazi, Characterization and properties of petroleum fractions, 2005)
log \( v_{38(100)} \)

\[
= 4.39371 - 1.94733K^2_w + 0.12769K^2_w + 3.2629 \times 10^{-4}API^2 - 1.18246 \times 10^{-2}K_wAPI
\]

\[+ 0.171617K^2_w + 10.9943(API) + 9.50663 \times 10^{-2}(API^2) - 0.860218K_w(API)
\]

\[\frac{(API) + 50.3642 - 4.78231K_w}{(API)}\]

(2.41)

The kinematic viscosities from equation (2.41) are in units of cSt (mm²/s). The Abbott method is not applicable to heavy oils. It is suitable for Watson factor range of 10-12.5 and API gravity range of 0-80. The method gives kinematic viscosities with an error in the range of 15-20% (Riazi, Characterization and properties of petroleum fractions, 2005).

In 1985, Twu came with a new model for prediction of kinematic viscosities of petroleum fractions. In the development of this method, Twu used a similar approach that he already employed in the prediction of molecular weights of petroleum fractions (1984). The principle is to predict the kinematic viscosities on the basis of their deviations from the kinematic viscosities of \( n \)-alkanes. In this method, the correlations are developed by using a perturbation theory. The equations proposed in this method are written as (Twu, 1985).

\[
T^* = T_b(0.533272 + 0.191017 \times 10^{-3}T_b + 0.779681 \times 10^{-7}T_b^2 - 0.284376 \times 10^{-10}T_b^3
\]

\[+ 0.959468 \times 10^{28}/10^{13\gamma}^{-1}\]

(2.42)

\[
\alpha = 1 - T_b/T^*_c
\]

(2.43)

\[
\ln(v^*_2 + 1.5) = 4.73227 - 27.0975\alpha + 49.4491\alpha^2 - 50.4706\alpha^4
\]

(2.44)

\[
\ln(v^*_1) = 0.801621 + 1.37179 \ln(v^*_2)
\]

(2.45)

\[
SG^* = 0.843593 - 0.128624\alpha - 3.36159\alpha^3 - 13749.5\alpha^{12}
\]

(2.46)
\[ \Delta SG = SG - SG^\circ \]  
\[ x = |1.99873 - 56.7394 / T_b^{1/2}| \]  
\[ f_1 = 1.33932 x \Delta SG - 21.1141 \Delta SG^2 / T_b^{1/2} \]  
\[ \ln(\nu_1 + 450 / T_b) = \ln(\nu_1^\circ + 450 / T_b) \left( \frac{1 + 2f_1}{1 - 2f_1} \right)^2 \]

The boiling points \((T_b)\) in above equations are in units of degree Rankin and the viscosities predicted from this method are in cSt (mm²/s). There were 563 data points of pure hydrocarbon components and petroleum fractions taken into account during the testing, and the results were obtained with an average error of 8.53%. The method covers the entire practical boiling point range of 580-1778°R (322-988 K) (Twu, 1985).

Moharam et al (1995) proposed a new correlation for predicting the kinematic viscosities of petroleum fractions. He correlated the desired property that is kinematic viscosity with the boiling temperature \((T_b)\), absolute temperature \((T)\) and specific gravity \((SG)\). The method is applicable for fractions with mid boiling point range of 353-823.15 K and measurement temperatures of 313-473K. The method is pretty accurate in predicting the viscosities which gives the results with an error of only 6.5%. The proposed equation is given as (Moharam H M, 1995)

\[ \ln \nu = A \exp \left[ \left( \frac{T_b}{T} \right) SG^B \right] + C \]
where,

\[ A = 1.0185 \]

\[ B = \frac{T_b}{305.078} - 0.55526 \]

\[ C = -3.2421 \]

\( T_b \) is the mid-boiling point of the fraction in Kelvin, \( T \) is the reference temperature at the kinematic viscosity to be estimated in Kelvin, \( SG \) is the specific gravity, \( \nu \) is the kinematic viscosity, in cSt (mm²/s).
3 LITERATURE REVIEW FOR EXPERIMENTAL METHODS

3.1 Boiling points and Distillation curves

For any pure component, a single temperature generally represents the boiling point for the component. However, a mixture of different components such as crude oil or petroleum fractions, where the boiling point differs from more volatile components to less volatile components. Therefore, the boiling points of a crude oil of unknown composition can be represented by a curve of different boiling point temperatures versus volume % of crude oil distilled (Riazi, Characterization and properties of petroleum fractions, 2005). A typical TBP curve is shown in figure 3.1.

![Figure 3.1 A typical true boiling curve for a petroleum fraction](image)

True boiling points curve is the presentation of volatility characteristics of petroleum fractions or crude oils (Daubert T E, 1997). The boiling point of the lightest hydrocarbon component is called as initial boiling point (IBP). The boiling of the heaviest hydrocarbon component is called as final boiling point (FBP). The temperature range between initial boiling point and final boiling
point is called boiling point range. For a particular petroleum fraction or crude oil, IBP and FBP points are not as reliable as the middle points of boiling range. In reality, it is very difficult to predict the final boiling point for heavy hydrocarbons. However, the FBP is estimated for the crude oil, the heaviest hydrocarbon may not vaporize at that temperature. If boiling points are estimated up to 70% of total crude oil feed, then the remaining 30% of crude is referred as a residue (Riazi, Characterization and properties of petroleum fractions, 2005). There are several methods to determine boiling points and develop true boiling point curve of petroleum fractions that are described below.

3.1.1 Laboratory TEST METHODS

3.1.1.1 ASTM D86

ASTM D86 is a batch distillation operation for determining and reporting boiling points of crude oils, and petroleum fractions. It is a simple and convenient method mostly applied to the distillation of motor gasoline, aviation gasoline, aviation turbine fuel, naphtha, kerosene, gas oil, distillate fuel oil, and similar petroleum products (Daubert T E, 1997). The distillation is conducted at atmospheric pressure, which required a very small amount of sample for the experiment. ASTM D86 operation is partly similar to a simple distillation operation; the system consists of apparatus such as a flask with attached glass tube condenser, temperature sensor on the top of the flask, and heating source. The system does not consist of packed or tray column (of minimum 15 theoretical plates) and reflux arrangement causes the operation not to attain a high degree of separation; therefore the boiling points from this standard method are not true boiling points of petroleum fractions. The boiling points from ASTM D86 need to be converted to the true boiling points.
3.1.1.2 ASTM D1160

ASTM D1160 is nothing but the vacuum distillation frequently used for the determination of boiling points of heavy hydrocarbons such as atmospheric residue after ASTM D86 method. As mentioned earlier ASTM D86 is an atmospheric distillation. All heavy hydrocarbons cannot be vaporized in the atmospheric distillation. Actually above 300°C in the atmospheric distillation, heavy hydrocarbons usually undergo a cracking process in which they start to break down in to lighter molecules. Therefore, there is a need to execute the further distillation at reduced pressure in order to avoid the cracking process. ASTM D1160 is the test method in which the distillation is carried out at reduced pressures without any significant cracking. The method is usually conducted at reduced pressures between 1 mm of Hg to 5 mm of Hg and a maximum temperature of 400°C. The system of ASTM D1160 is designed to obtained approximately one theoretical plate fractionation; therefore, the boiling point curves from ASTM D1160 are closer to true boiling point curves (ASTM D1160, 1998).

3.1.1.3 ASTM D2892

ASTM D2892 illustrates the procedure to carry out a distillation of stabilized crude oils or hydrocarbons at maximum temperature of 400°C. The procedure includes an atmospheric distillation as well as a reduced pressure distillation. ASTM D2892 system contains column of 14 to 18 theoretical plates and operates on reflux ratio of 5:1 which gives high degree of fractionation. Therefore, the distillation curves obtained from the system is in the form of true boiling point (TBP) and it can be expressed with mass or volume. ASTM D2892 is the laboratory standard which plays crucial part in estimation of crude oil value, determination of yields of fractions of different boiling points, and technical discussions for fixing the commercial values of petroleum products. Because of high degree of separation, the products obtained from
this laboratory technique can be used for analytical studies, engineering, and products quality evaluations (ASTM D2892, 1998).

3.1.1.4 ASTM D2887/ Stimulated Distillation by Gas Chromatography

ASTM D2887 is the test method describes the procedure to conduct gas chromatography experiments for determining the distillation curves of crude oils or petroleum fractions. The determination of distillation or boiling point curves of petroleum fractions by gas chromatography is called as simulated distillation (SD). The test method is capable of determining the boiling point up to 538°C but it is limited to initial boiling point greater than 55°C. The simulated distillation is simple, consistent, and reproducible that gives the distillation curves without any uncertainty (ASTM D2887, 1998).

Gas chromatography is the technique based on the volatility of hydrocarbon components in a petroleum fraction. In the analysis of GC, the components are separated according to their relative attraction towards a stationary or mobile phase. The injected sample to a GC column (stationary phase) is first converted to vapors which are then carried by a high purity carrier gas called effluents (mobile phase) (Riazi, Characterization and properties of petroleum fractions, 2005). As the effluents progresses through the column, the motion is hindered by a packing material in the column and walls of the column where an adsorption of components takes place. The adsorption process leads to the separation of different components from each other. The rate of progression of effluents depends on the rate of adsorption of components. And the rate of adsorption depends upon the type of molecules and the type of adsorbent material. Therefore, each type of component possesses different rate of progression which turn in the retention time (time taken by a component to pass through the GC column) is different for different type of components. When the components are discharged from the column, a detector records the type
of molecule and the respective retention time (Analytic Chemistry Research Foundation (ACRF), 2014). The record obtained from the chromatographic analysis is called chromatograph (Riazi, Characterization and properties of petroleum fractions, 2005). A typical chromatograph has shown below in figure 3.2.

*Figure 3.2-D2887 normal-paraffin calibration standard chromatogram. (Workman, 2008)*
3.1.2 True Boiling Point Method

The boiling curves from all ASTM test methods except ASTM D 2892 are not true boiling point curves for crude oil or fractions. TBP distillations require columns with 15-100 theoretical plates and high reflux ratios (5:1 or greater) to achieve accurate separation of components in a mixture. TBP distillations are difficult, time consuming, and expensive as compared to Laboratory test methods (Daubert T E, 1997). ASTM D2892 is only laboratory test method gives high degree of fractionation because the system has column with 15 theoretical stages and it operates at reflux ratio of 5:1. This method offers the compromise between efficiency and time so that the comparison of distillation data from different laboratories can occur (ASTM D2892, 1998).

3.1.3 Equilibrium Flash Vaporization

An equilibrium flash vaporization is an experiment where a vaporization of hydrocarbons is occurred at constant pressure to determine the relation between temperatures and volume percent of material vaporized. The curve obtained from this experiment is called an equilibrium flash vaporization curve (EFV). Each point on EFV curve represents a separate experiment; therefore numbers of experiments are required to define entire shape of EFV curve. According to API-TDB, at least five experiments are needed. The procedure to conduct the EFV experiment is seemed difficult as compared to other distillation methods that makes this experiment rarely used to determine distillation curve (Daubert T E, 1997). But the EFV curve plays an important role in design of mass transfer operation equipment such as distillation columns, vaporizers and condensers (Othmer, Ten Eyck, & Stanley, 1951). The typical EFV distillation curves along with ASTM D86 and TBP curves are shown in figure 3.3.
Figure 3.3-ASTM, True boiling Point, EFV curves for Naphtha- Kerosene blend.

With permission from (Daubert T E, 1997)
3.2 Density, Specific Gravity and API Gravity

The density, specific gravity and API gravity are crucial physical properties in characterization of any petroleum fraction. These three properties are measurable and closely related to each other. There is no need to measure all these properties separately; only a density or a specific gravity is needed to measure. If a specific gravity is known for a particular petroleum fraction, then it is possible to calculate the density as well as the API gravity for that fraction. In petroleum industry, specific gravity and API gravity measure at reference temperature of 15.56°C (60°F) and density usually reported at 20°C. There are some test methods and techniques available for the measurement of density, specific gravity and API gravity which are described below.

3.2.1 Laboratory Test Methods

3.2.1.1 ASTM D1298

ASTM D1298 is the test method describes the procedure to assess the density, specific gravity and API gravity of crude oils, petroleum fractions, petroleum and non-petroleum liquid mixtures or liquids which possess a raid vapor pressure of 1.79 bar (179 kPa). This test method uses a glass hydrometer to measure these properties. In ASTM D1298, the density, specific gravity and API gravity are measured at temperature of 15°C (60°F). When reporting the values of the properties, the density is noted in the unit of kilogram per liter at 15°C, and the specific gravity is noted with reference temperature for example, specific gravity (60/60°F). There is no need to state API gravity with the reference temperature because the reference temperature already included in the definition of API gravity (ASTM D1298, 1998). API gravity is defined in equation (2.2) as
API gravity, °API = \frac{141.5}{\text{SG (60/60°F)}} - 131.5

A hydrometer works on the principle of Archimedes that is buoyancy principle. The principle says that when a body of specific volume and weight is placed in a fluid, then the amount of fluid is displaced by the body is equal to the volume of the body as well as the weight of the body. The hydrometer is normally made of glass and has two main parts are a cylindrical stem and a bulb. A typical hydrometer is shown in figure 3.4. The cylindrical stem is a small diameter tube with rounded top mounted over the bulb. The stem consists of a long calibrated scale which is developed according the volume of fixed mass attached to the lower end of the bulb. The bulb is a larger diameter glass tube ballasted with weights (small metal spheres) at the end so that it floats upright in a liquid whose density or specific gravity is to be measured. The hydrometer is simply lowered into a liquid and the density, specific gravity or API gravity is directly measured from the scale. The hydrometers are also available in metal and plastic, but accuracy is an issue (Halit, 1999).

Figure 3.4-A typical hydrometer (Courtesy of Chemical Engineering Department at Dalhousie University)
3.2.1.2  *ASTM D4052*

ASTM D4052 is the test method that describes the procedure to determine the density and specific gravity of petroleum fractions and viscous oils at test temperatures between 15 to 35°C. The test method measures the properties with the help of digital density meter. The application of ASTM D4052 is limited to the liquids with vapor pressure below 0.8 bar (80 kPa) and viscosities below 15000 cSt (mm²/s) at the test temperature (ASTM D4052, 1998). The digital density meter works according to the law of harmonic oscillation in which a liquid whose density or specific gravity is to be measured is placed in a U sample tube and it is subjected to the electromagnetic force. Then the change oscillating frequency resulted by the change in mass of tube is used with calibration data to estimate the density (Furtado A, 2009). The oscillation type digital density meter is shown in figure 3.5.

![Figure 3.5-Oscillation type Digital Density Meter (Furtado A, 2009)](image-url)
3.2.1.3 ASTM D287

ASTM D287 gives a description of a procedure to measure the API Gravity of crude oils and petroleum fractions having a Reid vapor of 26 psi or less. The test method uses the API hydrometer for measuring the property. The hydrometer is same as described in section 3.2.1 earlier, but the scale on the stem of the hydrometer has been converted to API gravity scale. ASTM D287 is measured the API gravities of liquids at reference temperature of 15.5°C (60°F) (ASTM D287, 1998). The working principle and description of the hydrometer have mentioned in the section 3.2.1.

3.2.1.4 ASTM D1480

ASTM D1480 covers the procedure to estimate the density and specific gravity of liquids by using a Bingham Pycnometer. The technique is limited to liquids having vapor pressures less than 600 mm Hg and viscosities less than 40000 cSt (mm²/s). Moreover, it is designed to conduct experiments at any temperatures between 20 to 100°C. The method allows measuring the density at high temperatures but the precision does not apply at that time (ASTM Standard 1480, 2013). A pycnometer is a simple vessel having a fixed volume. The sample fluid is placed in to the pycnometer and the density is measured by weighing the weight of the filled vessel. The pycnometer is normally made of glass and is a simple vessel along with a long stopper has a capillary hole in it. A typical pycnometer is depicted in figure 3.6. The capillary in the stopper gives the determination of exact volume consequences the high resolution of density measurement. In a procedure, the first thing is to weight the empty vessel, and then filled with distilled water to measure the volume of the vessel. The vessel is then filled with sample liquid whose density is to be determined and weighted with high precision weighing machine. The
density is estimated by the ratio of the mass of the sample liquid and volume of the liquid (Halit, 1999).

![Figure 3.6-A typical pycnometer (Courtesy of Chemical Engineering Department at Dalhousie University)](image)

### 3.2.1.5 ASTM D1481

The test method is used to determine the density and specific gravity of the oils having viscosity range between 15 to 50 cSt at the temperature of 20°C. The method can be used to measure the density of melted waxes at elevated temperatures, but the condition is that the sample should not possess the vapor pressure of 0.13 bar (13 kPa) at that temperature. ASTM D1481 uses a lipkin bicapillary pycnometer to measure the density and specific gravity of oils. The lipkin bicapillary pycnometer is different from the bingham pycnometer; it is also made of glass but it has two side tubes in which the sample fluid has to be poured. The shape of lipkin bicapillary pycnometer has shown in figure 3.7. The oil sample is poured in the graduated side arms and allowed the pycnometer to reach equilibrium at the test temperature. Once the equilibrium is reached, the liquid levels in the side arms are noted and the pycnometer weighted. The density and specific
gravity of oil samples are determined from the volume of sample at the test temperature and the weight of the sample (ASTM Standard D1481, 2014).

Figure 3.7 - A lipkin bicapillary pycnometer (Courtesy of Chemical Engineering Department at Dalhousie University)
3.3 Kinematic Viscosity

Dynamic viscosity and kinematic viscosity are defined already in section 2.1. As mentioned earlier, both types of viscosities are important characterization parameters for petroleum fractions. The viscosity of the fluid plays a critical role in design of fuel injector, pumps, mass transfer equipment, and storage and transport facilities. As well as the viscosity is an essential parameter in selecting the appropriate lubricants for process equipment.

Dynamic and kinematic viscosities both are temperature and pressure dependent properties. The temperature is the most important parameter which affects the viscosity significantly. A small change in temperature can make changes in the viscosity values of a fluid. The small change in viscosity of the fluid is capable of developing huge impact on the properties of the petroleum fractions. Therefore, the accurate determination of the viscosity is essential (Lane & Henderson, 2004). There are some tests methods are discussed in upcoming sections.

3.3.1 Laboratory Test Methods

3.3.1.1 ASTM D445

The test method notifies the procedure to measure the kinematic viscosity of liquid petroleum fractions, both transparent and opaque. The method conducts the measurements of the viscosities with help of glass viscometers. The kinematic viscosities are determined by measuring the time required for a fixed volume of a liquid to flow under the influence of gravity through the capillary of a calibrated viscometer. The kinematic viscosity is the product of the measured time to flow the liquid and the calibration constant. It is expressed in the unit of cSt ($\text{mm}^2/\text{s}$). The dynamic viscosity can be calculated by multiplying the kinematic viscosity ($\nu$) by the density of the liquid ($\rho$) (ASTM 445, 1998). In the petroleum industry, the kinematic viscosities are usually measured at reference temperature of 38°C (100°F) and 99°C (210°F) (Riazi, Characterization
and properties of petroleum fractions, 2005). The type of glass viscometer is generally used in ASTM D445 which has shown in figure 3.8.

![Figure 3.8-A typical suspended level glass viscometer (Cannon Instrument Company, 2009)](image)

### 3.3.1.2 ASTM D2893

The test method is normally conducted to determine the low shear-rate viscosities of heavy petroleum fractions with the help of Brookfield Viscometers. The viscometer rotates a spindle in a fluid and measures the torque required to overcome the viscous resistance to make movement (Brookfield Engineering Laboratories, Inc.). The dynamic viscosity can be calculated from the measured torque multiplied by the calibrated factor for an appropriate spindle type. A Brookfield viscometer is shown in figure 3.9. With the help of ASTM D2893, it is possible to measure the viscosities in the range of 500 to 900 000 mPa·S (milliPascal-Second).
Figure 3.9 - A Brookfield viscometer along with spindle set.

(Courtesy of Chemical Engineering Department at Dalhousie University)
4 EXPERIMENTAL SYSTEMS AND PROCEDURES

4.1 Boiling Points/ Distillation Curves

In previous section, we discussed the different methods to determine boiling points or distillation curves for crude oils and petroleum fractions such as ASTM D86, ASTM D1160, ASTM D2892, etc. Among these methods, ASTM D2892 is chosen to develop a boiling point curve for Texas West Intermediate crude oil because ASTM D2892 is only the procedure by which true boiling point curve can be achieved for crude oil. In this section, the distillation assembly for ASTM D2892, and the experimental procedure are described.

4.1.1 ASTM D2892

ASTM D2892 is the test method developed by ASTM (American Standards and Testing Materials) International organization to achieve the boiling point curve which closer to the true boiling point curve for any stabilized crude oils or petroleum fractions. To develop actual true boiling point curve for crude oil is a complex procedure which normally requires 15-100 theoretical plates column to achieve a high degree of separation and it is time consuming process. Therefore, ASTM D2892 is developed at laboratory scale which offers a compromise between efficiency and time in order to get the true boiling point curve. The test method helps to obtain the boiling points up to the final boiling point of 400°C AET (Atmospheric Equivalent Temperature). The boiling points obtained from this method can be graphed against either percent volume or percent weight (ASTM D2892, 1998).

Experimental Setup

In ASTM D2892 test method, the distillation operation is used to determine the boiling points of crude oils or petroleum fractions. The distillation assembly and whole experimental system is
demonstrated in figure. 4.1. As shown in the figure, the fractionating column (packed column) is mounted on a flask having a maximum capacity of 4.8 liters. The flask is provided with an electric heating system where the heat input can be controlled manually or automatically.

*Figure 4.1-Distillation assembly system according to ASTM D2892
(Courtesy of Chemical Engineering Department at Dalhousie University)*
The fractionating column and the half portion of the flask are also surrounded with heating mantles which controls the temperature in the column to avoid an unnecessary heat loss. The fractionating column is designed to have a reflux valve and a condenser attached to the top of the column. The column is also configured with a product outlet, where a product cooler is attached. The condenser and the product cooler both are provided with a cooling water to condense product vapors into liquids. The temperature of the cooling water is controlled by a cooling system. A glycol is used as a heat exchanger fluid in the cooling system. At the end of the product cooler, product receivers are attached to collect different fractions according to their respective temperature ranges. The experimental system is also given with cold gas traps where initial low boiling point vapors or gases are collected by maintaining the temperature below 0°C in it. The system allows conducting the distillation at atmospheric pressure as well as at reduced pressure (vacuum distillation). Accordingly a vacuum pump is given in the system to run the vacuum distillation. The vacuum connections are given at the top of condenser and the top of the receivers so that whole system will be cover under vacuum during the operation. The vacuum connection is attached at the top of the condenser to avoid the product vapor loss. During the vacuum distillation, the vapor temperatures observed at the top of the fractionating column are usually converted to an Atmospheric Equivalent Temperature (AET) for simplification and continuation of true boiling curves.

**Atmospheric Equivalent Temperature (AET)**

The observed distillation temperatures can be converted to AET using the tables given in ASTM D2892 or using following equation (ASTM D2892, 1998)
AET = \frac{748.1A}{1} - 273 \quad \text{(4.1)}
\frac{1}{T + 273} + 0.3862A - 0.00051606

where:
AET = \text{atmospheric equivalent temperature,} °C,
T = \text{observed vapor temperature,} °C,

A = \frac{5.143324 - 0.972546 \log P}{2579.329 - 95.76 \log P} \quad \text{(4.2)}

P = \text{pressure, between 0.27 and 101.3 kPa, or}

A = \frac{5.994296 - 0.972546 \log p}{2663.129 - 95.76 \log p} \quad \text{(4.3)}

P = \text{pressure, between 2 and 760 mm Hg.}

\textit{Experimental Procedure:}

The flask has a minimum capacity of 1.2 liters and maximum of 4.8 liters. According to the availability of WTI crude oil, batches of 1.2 liters of crude oil were chosen for the distillation experiment. The distillation operation was carried out at three different pressures are 760 mm Hg (atmospheric pressure), 100 mm Hg (under vacuum), and 2 mm Hg (under lowest vacuum). The reason behind the distillation experiment at three different pressures is to get more and more fractions so the boiling point curve would reach up to the final boiling point of 382.4° C. The pressure of 2 mm Hg is the lowest pressure that can be applied by using the vacuum pump in the system. There were three batches of same volumes processed in the system to validate the data (boiling points) obtained from the system.

Before charging the crude oil in the flask, the density of the oil was determined using ASTM D1298. Once the batch was charged and the heating was started, the distillation operation
initiated by a debutanization process where normally low volatile components are collected in the gas trap and gases like H\textsubscript{2}S, and N\textsubscript{2} are stripped off. But low volatile components were not collected during this distillation of WTI crude oil; this might be because of absence of low volatile components at that stage of the crude oil. During the debutanization, the temperature in the condenser and the product cooler was maintained lower than -20°C.

*Distillation at atmospheric pressure (760 mm Hg):*

During the distillation at atmospheric pressure, the boil up rate 75% of maximum was applied initially but later it was adjusted according to the product recovery. Also, the reflux ratio of 5:1 was preserved for the entire atmospheric distillation. The temperature of -20°C was maintained in the condenser as well as in the cooler until the vapor temperature of 65°C was achieved or the collection of first fraction was started. When these conditions were obtained, the temperatures in the condenser and in the cooler were brought to ambient temperature of 20°C. The reason behind this deed was to sustain the appropriate temperature environment in the fractionating column; otherwise it would increase the heat consumption and affect the fractions recovery. As the distillation had progressed, the fractions were collected according to their cut points (boiling point ranges). At the end of each fraction or at the cut point the following observations were noted

1. Total volume collected, ml
2. Time in minutes
3. Vapor temperatures at start and end points of the fraction, °C
4. Temperature of the boiling liquid in the flask, °C
The fractions were collected until the maximum vapor temperature was reached. With the help of this distillation, three fractions were obtained until 200°C which was the maximum vapor temperature noted. The remaining amount of the crude oil after the atmospheric distillation is called atmospheric residue. After reaching the maximum vapor temperature the heating and the reflux valve were turned off and the whole system was allowed to cool down.

*Distillation at reduced pressure of 100 mm Hg (13.7 kPa):*

To acquire the fractions beyond 200°C, the distillation was continued with the atmospheric residue at reduced pressure of 100 mm Hg. The pressure of 100 mm Hg was controlled by using the vacuum pump in the system. The vacuum of 100 mm Hg was developed gradually in the whole system before liquid started heating. Once the vacuum was maintained in the system, the heating started at boil up rate 75% of maximum and the fractionating column was put under a total reflux condition to attain equilibrium. When the equilibrium was attained, the reflux ratio of 2:1 was applied. The temperature conditions in the condenser and the product cooler were maintained at ambient temperature throughout the vacuum distillation. The fractions were collected according to their cut points or boiling point ranges. At the end of each fractions the following observations were noted

1. Total volume collected, ml
2. Time in minutes
3. Vapor temperatures at start and end points of the fraction, °C
4. Temperature of the boiling liquid in the flask, °C
5. AET (Atmospheric Equivalent Temperature) in °C
In this distillation, four fractions were obtained until 320°C which was the maximum vapor temperature noted. The residue remaining after the vacuum distillation is called as vacuum residue.

*Distillation at reduced pressure of 2 mm Hg:*

To achieve further boiling points beyond 320°C for the crude oil, the distillation was extended further at reduced pressure of 2 mm Hg. The procedure and observations taken for fractions were same as the earlier vacuum distillation’s procedure and observations. In this distillation, three more heavy fractions were successfully collected and the maximum vapor temperature of 382.4°C was identified. After completion of the distillation process, the residue was taken out, weighted, and density and viscosity of the residue were measured.

By using above three distillations, total 11 fractions were successfully distilled out and their respective boiling point ranges and volume collected were also noted correctly. The masses of all fractions were measured. In order to develop the true boiling point data for the crude oil, the boiling point ranges, volumes of fractions, masses of fractions, and volume or mass cumulative percentages for all fractions were reported in the observation sheet.
4.2 Density or Specific Gravity Measurement

As discussed in section 3.2, the density, specific gravity and API gravity are measureable properties play crucial role in the characterization of petroleum fractions. These three properties are interrelated so measurement of any one of the properties is enough to estimate remaining two properties. With knowledge of prior sentence and availability of a hydrometer type in the lab, the decision of measuring of the specific gravities by using hydrometer was made. As studied earlier ASTM D1298 describes the procedure to measure the specific gravity by using the hydrometer technique; therefore ASTM D1298 was used.

4.2.1 ASTM D1298

As mentioned earlier in the section 3.2, this test method is useful for measurement of density, specific gravity, or API gravity of liquids by using Hydrometer technique. The test method details the procedure, apparatus setup, calculation, report and many more information in relation to the measurement of the properties.

Experimental Setup and Procedure:

In the measurement of specific gravities of petroleum fractions, the hydrometer (specific gravity type), temperature bath, a cylindrical container to place a petroleum fraction, and thermometer were used. The arrangement of apparatus is shown in figure 4.2. Firstly, the water temperature bath was prepared and maintained at reference of 15°C (60°F). Once the bath was ready, the petroleum fraction bearing cylindrical container was placed in the center of the bath and allowed the fraction container to acquire the surrounding temperature for some time. When the fraction was cooled down to the reference temperature, the hydrometer was lowered into the fraction and left it to suspend freely in the liquid. At one time the hydrometer was come to rest, freely floating
away from the walls of the container. When the hydrometer was floating freely, a reading was observed on the cylindrical stem of the hydrometer. The reading is the point where the liquid level touches at that point on the scale of the stem. As seen earlier in section 3.2, the scale in the cylindrical stem is already calibrated to the specific gravity values, so that the reading observes on the scale of the stem is directly the specific gravity of that liquid. Once the specific gravity of the petroleum fraction was estimated, the density of the fraction was calculated by multiplying the specific gravity of the fraction to the density of water, and the API gravity of the fraction was calculated by the equation (2.2). By using the same method and procedure, the specific gravities, densities, and API gravities for all petroleum fractions and the crude oil were determined and noted.

Figure 4.2-Experimental setup for measurement of specific gravity using hydrometer

(Courtesy of Chemical Engineering Department at Dalhousie University)
4.3 Kinematic Viscosity Measurement

The definition of dynamic viscosity and kinematic viscosity, and the different test methods for measurement of kinematic viscosity are discussed earlier in section 3.3. The both viscosities dynamic and kinematic execute an important role in the characterization of petroleum fractions. In the measurement of kinematic viscosities of all petroleum fractions, Ubbelohde glass capillary viscometers were used. The estimation of the viscosity of the lowest vacuum residue was measured by the Brookfield dial viscometer.

4.3.1 ASTM D445

ASTM D445 is the test method which describes the procedure to assess the kinematic viscosities of petroleum fractions by using the Ubbelohde glass capillary viscometers. The range of kinematic viscosities covered by this test method is 0.2 to 300,000 mm²/S. Kinematic viscosities of all petroleum fractions (2-11) except fraction no.1 were estimated by using this test method. The kinematic viscosities of all fractions were determined at the reference temperature of 38°C. To maintain the reference temperature of petroleum fractions the KV4000 Digital Constant Temperature Kinematic Viscosity Bath was used. It is designed to perform the kinematic viscosity tests with glass viscometers according to ASTM standards and related test specifications (Koehler Instrument Company, Inc.)
Experimental setup and Procedure:

To measure the kinematic viscosity of particular petroleum fraction the following apparatus were required:

- a kinematic viscosity bath
- thermometer
- stopwatch
- Ubbelohde glass viscometer.

These apparatus were also labeled in figure 4.3. The figure is showing the experimental setup for the measurement of kinematic viscosities of light and medium petroleum fractions. A distilled
water was used as the bath medium. The kinematic viscosity of each fraction was measured at temperatures 20, 25, 30, 35, 38, 45°C. Firstly, the bath was filled with the distilled water and maintained at the specific temperature (20°C) at which the viscosity was to be measured first. On the other side, an appropriate glass viscometer was selected for a petroleum fraction of which the viscosity was to be measured. The selection was made on the basis of a time required for the fraction to flow through the capillary of the viscometer. After selecting the correct viscometer, the viscometer was prepared with the petroleum fraction. Once the specific temperature was reached in the bath, the petroleum fraction bearing glass viscometer was placed in to the bath with a help of steel holder. Then the viscometer was allowed for some time to attain the bath temperature. When the temperature was attained by the fraction, with a help of suction bulb the liquid was pulled (imbibed) in the capillary arm of the viscometer up to 7mm above the first timing mark. And then the liquid was realized to flow freely from the first timing mark to the second mark in the capillary arm. With the sample liquid was flowing freely, the time was measured for the liquid meniscus to pass from the first mark to second mark. The flow time ($t_1$) for the petroleum fraction was recorded and it was further used to calculate the kinematic viscosity.

**Calculation:**

The kinetic viscosity ($\nu$) for the fraction was calculated by multiplying the flow time ($t_1$) to the viscometer constant ($C$),

$$\nu = C \times t_1$$  \hspace{1cm} (4.1)

where,

$\nu$ = the kinematic viscosity of the petroleum fraction, mm²/S,
$t_1$ = the flow time, Sec,

$C$ = the calibrated viscometer constant.

The dynamic viscosity ($\mu$) was calculated with the help of the kinematic viscosity ($\nu$) of the petroleum fraction and the density ($\rho$) of that fraction by using following equation,

$$\mu = \nu \times \rho \times 10^{-3} \quad (4.2)$$

where,

$\mu$ = the dynamic viscosity of the petroleum fraction, mPa S,

$\rho$ = the density of the petroleum fraction, Kg/m$^3$,

$\nu$ = the kinematic viscosity of the petroleum fraction, mm$^2$/S.

The same procedure and calculations were repeated for all petroleum fractions to determine the kinematic viscosities as well as the dynamic viscosities.
4.3.2 **ASTM D2893**

ASTM D2893 details the process to estimate the dynamic viscosities as well as the kinematic viscosities of heavy petroleum fuels or residues by using the brook field viscometer. The residue left after last stage of distillation (2mm Hg) was too thick and imagined that it would have high viscosity values; therefore the brook field viscometer was used to measure the viscosities of the residue. The viscosities of Texas west intermediate crude oil were also measured by this method. The viscosities of a residue and the crude oil were measured at the reference temperature of 38° C.

*Brook field Digital Viscometer:*

The brook field viscometer is usually used to measure the dynamic viscosities of heavy petroleum fractions or residues. The viscometer rotates a spindle in a fluid and measures the torque required to overcome the viscous resistance to make movement. The driving movement of the spindle is induced by a beryllium copper spring; the amount of extend to which the spring is wound, indicated by the digital display which is directly proportional to the viscosity of the fluid. The viscosity of the fluid also depends on the spindle speed and the spindle size and shape. To calculate the viscosity, multiply the reading noted on the viscometer dial by the factor which is specially developed for the viscometer according to the spindle speed and the spindle size. For a fluid of known viscosity, the resistance to the rotation of a spindle increases as the spindle speed and the spindle size increases. Therefore, to obtain the maximum viscosity range the smallest spindle at lowest speed is recommended, while for the minimum viscosity range the largest spindle at highest speed is recommended (Brookfield Engineering Laboratories, Inc.). An experimental setup for the measurement of kinematic viscosity of the residue using brook field viscometer has shown in figure 4.4.
Experimental Setup and Procedure:

The experimental setup for the measurement of kinematic viscosity of the residue is shown as in figure 4.4. As a part of equipment setup, the Brookfield viscometer was already mounted on the Brookfield laboratory stand. A guard leg was then screwed to the viscometer and an appropriate spindle was attached to lower shaft of the viscometer. After that the viscometer was leveled by referring the bubble level on the back of the instrument. On the other side, the residue sample was taken in a 600 ml beaker and brought to the reference temperature of 38°C by using a water bath. Once the sample was reached to the reference temperature, the spindle was inserted in the center of the beaker until the fluid level was at immersion mark in the spindle’s shaft. The power of the viscometer was then switched “on”, the digital display was set to zero and a spindle speed
was selected. Once the speed was set, the motor switch was turned “on” to rotate the spindle in the sample fluid. The spindle was allowed to rotate in the sample for some time until the indicated reading was stabilized. The time required for stabilization depends upon the speed of the spindle and the nature of the sample. The stabilized reading was then noted and further used to calculate the dynamic viscosity of the residue sample. To calculate the viscosity of the residue, the noted reading was multiplied by the factor appropriate to the spindle and speed combination used. Further, the kinematic viscosity was calculated by using equation (2.5). The same procedure was repeated for the measurement of the viscosities of Texas West Intermediate crude oil.

4.4 Error and Accuracy of Equipment

<table>
<thead>
<tr>
<th>Measured Property</th>
<th>Apparatus</th>
<th>Accuracy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distillation Temperature Ranges</td>
<td>Thermocouple</td>
<td>± 0.1°C</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>Hydrometer</td>
<td>± 0.001</td>
</tr>
<tr>
<td>Kinematic Viscosity</td>
<td>Glass Viscometer</td>
<td>± 0.003 cSt or mm²/s</td>
</tr>
<tr>
<td></td>
<td>Brook Field Viscometer (Measurement of Torque)</td>
<td>± 0.1 Nm</td>
</tr>
<tr>
<td>Reference Temperature</td>
<td>Thermometer</td>
<td>± 1.0°C</td>
</tr>
</tbody>
</table>
5 EXPERIMENTAL RESULTS AND DISCUSSION

5.1 True boiling Points

The experimental methods and procedures of all distillation operations were discussed in section 4.1. Those operations were required to acquire the true boiling point data for the crude oil. In the distillation, one atmospheric distillation and two vacuum distillations at different pressures were conducted to achieve maximum boiling points for the crude oil. The distillation operations were executed according to ASTM D 2892. The whole distillation operation was repeated for three times with the same volume of the crude oil to examine the consistency of the equipment system. The volumes collected according to the respective boiling point ranges and respective operating pressures at which the different fractions were collected are shown in table 5.1.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Operating Pressure, mm of Hg</th>
<th>Temp Range In K</th>
<th>Volume collected, ml</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Batch 1</td>
</tr>
<tr>
<td>1</td>
<td>760</td>
<td>343-373</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>760</td>
<td>373-433</td>
<td>48</td>
</tr>
<tr>
<td>3</td>
<td>760</td>
<td>433-473</td>
<td>79</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>343-473</td>
<td>68</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>473-523</td>
<td>131</td>
</tr>
<tr>
<td>6</td>
<td>100</td>
<td>523-573</td>
<td>120</td>
</tr>
<tr>
<td>7</td>
<td>100</td>
<td>573-593</td>
<td>18</td>
</tr>
<tr>
<td>8</td>
<td>2</td>
<td>473-593</td>
<td>68</td>
</tr>
<tr>
<td>9</td>
<td>2</td>
<td>593-633</td>
<td>75</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>633-655</td>
<td>112</td>
</tr>
<tr>
<td>Residue</td>
<td></td>
<td>655&lt;</td>
<td>448</td>
</tr>
</tbody>
</table>

As shown in table 5.1, during the atmospheric distillation an approximately 17.5 % of total crude oil feed is recovered, while around 45 % and 60 % of crude oil charged is collected during vacuum distillations of 100 mm of Hg and 2 mm of Hg respectively. The fractions up to 200°C
(473 K) are obtained in atmospheric distillation and further fractions until 382° C (655 K) are obtained with the help of vacuum distillations. Normally, the heavy hydrocarbons in crude oil undergo a cracking process beyond 300° C; the cracking process where heavy hydrocarbons start to decompose into small hydrocarbon chains. To avoid this decomposition of hydrocarbons, the further distillation operations after atmospheric (the distillation above 300° C) are conducted under vacuum or at reduced pressure. The vacuum distillation not only helps to avoid the cracking of hydrocarbons, but also reduces the boiling points of heavy hydrocarbons in order to achieve more and more boiling points for the crude oil without any significant cracking.

As shown in table 5.1, the boiling points until 60% point are available from the ASTM method or TBP method; the remaining 40% points are not available. But the boiling point curve up to 90 or 95% points is important for the processing of the crude oil as well as for the characterization of petroleum fractions. To extend this TBP curve till 95% point, the Two-Parameter Distribution Model developed by Riazi (1989) is used. The equation of the model is already discussed in section 2.2.1.2. Either a linear progression or an excel solver can be used to solve the model equation. The boiling points obtained up to 95% point are shown in table 5.2.
Table 5.2-Prediction of complete TBP curve

<table>
<thead>
<tr>
<th>$T_{act}$</th>
<th>Cum Volume %</th>
<th>$T_{cal}$ Linear Progression</th>
<th>Excel Solver</th>
</tr>
</thead>
<tbody>
<tr>
<td>373.15</td>
<td>0.53</td>
<td>373.80</td>
<td>377.69</td>
</tr>
<tr>
<td>433.15</td>
<td>5.33</td>
<td>424.01</td>
<td>423.31</td>
</tr>
<tr>
<td>473.15</td>
<td>17.28</td>
<td>488.04</td>
<td>485.64</td>
</tr>
<tr>
<td>523.15</td>
<td>26.67</td>
<td>527.04</td>
<td>524.94</td>
</tr>
<tr>
<td>573.15</td>
<td>36.78</td>
<td>565.89</td>
<td>564.82</td>
</tr>
<tr>
<td>593.15</td>
<td>45.06</td>
<td>597.29</td>
<td>597.49</td>
</tr>
<tr>
<td>633.15</td>
<td>51.22</td>
<td>621.19</td>
<td>622.61</td>
</tr>
<tr>
<td>655.55</td>
<td>60.42</td>
<td>658.87</td>
<td>662.57</td>
</tr>
<tr>
<td>-</td>
<td>70.00</td>
<td>702.95</td>
<td>709.84</td>
</tr>
<tr>
<td>-</td>
<td>80.00</td>
<td>759.30</td>
<td>770.98</td>
</tr>
<tr>
<td>-</td>
<td>90.00</td>
<td>841.45</td>
<td>861.36</td>
</tr>
<tr>
<td>-</td>
<td>95.00</td>
<td>912.20</td>
<td>940.22</td>
</tr>
</tbody>
</table>

The graphical curves of predicted boiling points and experimental boiling points versus cumulative volume percent are shown in figure 5.1.

![Figure 5.1-Experimental boiling point and predicted boiling point curves for the crude oil](image-url)
Emergencies Science and Technology Division of Environment Canada carried out a study on Texas West Intermediate crude oil in order to estimate the physical properties, the hydrocarbon and metal compositions, TBP Curve, etc. (Environment Canada, 1994). The TBP curve from the above study has been used as a reference standard to validate my experimental observations especially TBP curve. According to that the reference TBP curve and the TBP curve that obtained from my experimental observations have been plotted on a same graph in order to compare with each other. The comparison of the both TBP curves is shown in figure 5.2.

![Figure 5.2-Comparison of the reference TBP Curve and Experimental TBP Curve](image)

In figure 5.2, the line with squares is indicating the reference TBP curve while remaining three lines are showing the experimental TBP curves. The reference TBP curve starts from 313.15 K (40° C) and ends at 923.15 K (650° C) while the experimental TBP curve is from 373.15 K
(100°C) up to 959.65 K (686.5°C). The TBP curve has started late as compared to the reference
TBP curve, this situation is because of an absence of light hydrocarbons in the crude oil. The
light hydrocarbon might have flashed off earlier during the storage or transportation of the crude
oil prior to the distillation of the crude oil. However, the experimental TBP curve started lately
where only 0.46% volume collected at 373.15 K (100°C), the curve further followed the typical
TBP curve in comparison with the reference curve. There is a hypothetical curve has been
developed in figure 5.2, which is shown by a multiplication sign. If the missing percentages of
light hydrocarbons is considered to the crude oil sample, then the experimental curve for WTI
crude oil would be as the hypothetical curve. The reason behind the presentation of the
hypothetical curve is to show that the experimental curve has started lately is only because of
absence of the light hydrocarbons in the crude oil sample.
5.2 Density Curve

Specific gravities experiments were performed using the hydrometer technique and estimation of the densities and API gravities from the observed specific gravities were discussed in section 4.2. As briefed in the literature section, the specific gravity at 15.5°C, density, and API gravity are the important characterization parameters for any petroleum fractions. With respect to, the specific gravities were measured at the reference temperature of 15.5°C, and the density, and the API gravities were calculated for all distilled petroleum fractions.

Table 5.3-the specific gravities, density, and API gravities according to petroleum fractions

<table>
<thead>
<tr>
<th>FRACTIONS</th>
<th>TEMPERATURE RANGES In K</th>
<th>DENSITY, at 15.5°C kg/m^3</th>
<th>SP.GRAVITY, at 15.5°C</th>
<th>API Gravity, In °API</th>
</tr>
</thead>
<tbody>
<tr>
<td>CUT 1</td>
<td>343-373</td>
<td>774</td>
<td>0.774</td>
<td>51.29</td>
</tr>
<tr>
<td>CUT 2</td>
<td>373-433</td>
<td>780</td>
<td>0.780</td>
<td>49.91</td>
</tr>
<tr>
<td>CUT 3</td>
<td>433-473</td>
<td>802</td>
<td>0.802</td>
<td>44.93</td>
</tr>
<tr>
<td>CUT 4</td>
<td>343-473</td>
<td>830</td>
<td>0.830</td>
<td>38.88</td>
</tr>
<tr>
<td>CUT 5</td>
<td>473-523</td>
<td>840</td>
<td>0.840</td>
<td>36.95</td>
</tr>
<tr>
<td>CUT 6</td>
<td>523-573</td>
<td>870</td>
<td>0.870</td>
<td>31.05</td>
</tr>
<tr>
<td>CUT 7</td>
<td>573-593</td>
<td>883</td>
<td>0.883</td>
<td>28.73</td>
</tr>
<tr>
<td>CUT 8</td>
<td>473-593</td>
<td>892</td>
<td>0.892</td>
<td>27.13</td>
</tr>
<tr>
<td>CUT 9</td>
<td>593-633</td>
<td>905</td>
<td>0.905</td>
<td>24.85</td>
</tr>
<tr>
<td>CUT 10</td>
<td>633-655</td>
<td>917</td>
<td>0.917</td>
<td>22.76</td>
</tr>
<tr>
<td>RESIDUE</td>
<td>655&lt;</td>
<td>934</td>
<td>0.934</td>
<td>19.85</td>
</tr>
</tbody>
</table>

In table 5.3, the measured and calculated properties are reported with respect to their fraction numbers and temperature ranges. Table 5.3 shows that the specific gravities are varying from 0.7741 for the lightest fraction to 0.9349 for the residue which is the heaviest fraction acquired in my study. The specific gravities and densities are increasing continuously with the boiling points of the fractions. The fractions acquired are becoming more and more dense or heavy as the distillation of crude oil approaching towards the end of the process. This trend is usually
occurred because of increasing the share of heavy hydrocarbons and decreasing the share of light hydrocarbons continuously in petroleum fractions of crude oil. But the trend is different in the case of API gravities of the fractions, normally the API gravity values more for light hydrocarbons and lower for heavy hydrocarbons. As seen in table 5.3, the API gravities varies from 51.3 for light petroleum fraction to ~ 20 for the residue; the API gravity values are continuously decreasing as the fractions are becoming heavier. The API gravity was observed for the residue is 19.85.

As discussed in section 2.2.2.1, the density at 20°C ($\rho_{20}$) is the characterization parameter, which can be predicted by using the specific gravities at 15.5°C. Different correlations for the predictions of the density were also discussed in that sections. The densities at 20°C for the petroleum fractions were calculated from the specific gravities of the fractions measured at 15.5°C using equations (2.15) and (2.18), and thumb rule. The predicted densities are shown in table 5.4.

### Table 5.4-Prediction of densities at 20°C

<table>
<thead>
<tr>
<th>FRACTIONS</th>
<th>DENSITY AT 20°C, kg/m³</th>
<th>Eq.(2.15)</th>
<th>Eq.(2.18)</th>
<th>Thumb Rule</th>
</tr>
</thead>
<tbody>
<tr>
<td>CUT 1</td>
<td>770.188</td>
<td>769.527</td>
<td>770.230</td>
<td></td>
</tr>
<tr>
<td>CUT 2</td>
<td>776.139</td>
<td>775.583</td>
<td>776.100</td>
<td></td>
</tr>
<tr>
<td>CUT 3</td>
<td>798.328</td>
<td>797.757</td>
<td>797.990</td>
<td></td>
</tr>
<tr>
<td>CUT 4</td>
<td>827.071</td>
<td>826.321</td>
<td>826.347</td>
<td></td>
</tr>
<tr>
<td>CUT 5</td>
<td>836.652</td>
<td>835.907</td>
<td>835.800</td>
<td></td>
</tr>
<tr>
<td>CUT 6</td>
<td>867.413</td>
<td>866.579</td>
<td>866.148</td>
<td></td>
</tr>
<tr>
<td>CUT 7</td>
<td>880.130</td>
<td>879.303</td>
<td>878.693</td>
<td></td>
</tr>
<tr>
<td>CUT 8</td>
<td>889.096</td>
<td>888.230</td>
<td>887.540</td>
<td></td>
</tr>
<tr>
<td>CUT 9</td>
<td>902.210</td>
<td>901.301</td>
<td>900.475</td>
<td></td>
</tr>
<tr>
<td>CUT 10</td>
<td>914.613</td>
<td>913.703</td>
<td>912.713</td>
<td></td>
</tr>
<tr>
<td>RESIDUE</td>
<td>932.394</td>
<td>931.672</td>
<td>930.256</td>
<td></td>
</tr>
</tbody>
</table>
Table 5.4 shows the comparison of between the predictions of the densities obtained from the three different correlations. The difference between the predicted values of three correlations is comparatively very small. Riazi (2005) evaluated these three correlations with the help of experimental results, and he found that all three correlations had given good results with an average deviation less than 0.5%. But he then selected equation (2.15) as the most accurate correlation for the prediction of densities on the basis of the smallest average deviation given (Riazi, Characterization and properties of petroleum fractions, 2005).

On the basis of the discussion made above, the densities ($\rho_{20}$) acquired from equation (2.15) have been considered as actual (real) densities ($\rho_{20}$) for the petroleum fractions. And these density values ($\rho_{20}$) have been used further to develop the complete density curve for the crude oil in my study.

<table>
<thead>
<tr>
<th>Cum Volume %</th>
<th>Density</th>
<th>Calculated Density, $\rho_{cal}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Distribution Model</td>
</tr>
<tr>
<td>0.53</td>
<td>770.189</td>
<td>764.605</td>
</tr>
<tr>
<td>5.33</td>
<td>776.139</td>
<td>781.101</td>
</tr>
<tr>
<td>17.28</td>
<td>798.328</td>
<td>811.316</td>
</tr>
<tr>
<td>26.67</td>
<td>836.652</td>
<td>833.387</td>
</tr>
<tr>
<td>36.78</td>
<td>867.413</td>
<td>857.666</td>
</tr>
<tr>
<td>45.06</td>
<td>880.310</td>
<td>878.782</td>
</tr>
<tr>
<td>51.22</td>
<td>902.208</td>
<td>895.696</td>
</tr>
<tr>
<td>60.42</td>
<td>914.613</td>
<td>923.716</td>
</tr>
<tr>
<td>70</td>
<td>-</td>
<td>958.489</td>
</tr>
<tr>
<td>80</td>
<td>-</td>
<td>1005.819</td>
</tr>
<tr>
<td>90</td>
<td>-</td>
<td>1080.135</td>
</tr>
<tr>
<td>95</td>
<td>-</td>
<td>1148.768</td>
</tr>
</tbody>
</table>
As seen in table 5.5, the densities ($\rho_{20}$) are only available up to 60% of cumulative volume; further densities are not available. Therefore, the distribution model developed by Riazi (1989) was employed to obtain the densities ($\rho_{20}$) up to 95% point. In table 5.5, the predicted values of the densities ($\rho_{20}$) are shown in the last column. Also, the predicted complete density curve is presented in figure 5.3 along with the actual density values. Figure 5.3 shows the density curve is extended after 60% until 95% point, and the predicted complete density curve is in good relation and in trend with the actual density values ($\rho_{20}$).
5.3 Molecular Weight Curve

In section 2.2.2.2, the discussion has made over how molecular weights are important for petroleum fractions and how the molecular weights can be predicted accurately using different correlations. The molecular weight is not a bulk property. However, it can be estimated using experimental methods, but the laboratory experimental methods are expensive, time-consuming, and difficult. It is not a feasible option all the time to employ the experimental methods for estimating the molecular weights. Therefore, instead of the experiments the molecular weights can be predicted accurately from available measured properties such as boiling points, specific gravity, viscosity, or Watson factor. A variety of prediction methods have been developed to predict the molecular weights. A few of them are selected and have been used to estimate the molecular weights in my study. The molecular weights of the petroleum fractions were estimated by using prediction methods such as Riazi-Daubert, Lee-Kesler, Goossens, Winn nomogram, and Twu.

<table>
<thead>
<tr>
<th>Fractions</th>
<th>$T_{bi}$</th>
<th>Molecular Weight, M</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Kelwin</td>
<td>Riazi-Daubert</td>
</tr>
<tr>
<td>1</td>
<td>363.15</td>
<td>94.30</td>
</tr>
<tr>
<td>2</td>
<td>403.15</td>
<td>115.35</td>
</tr>
<tr>
<td>3</td>
<td>453.15</td>
<td>144.77</td>
</tr>
<tr>
<td>4</td>
<td>473.15</td>
<td>155.62</td>
</tr>
<tr>
<td>5</td>
<td>498.15</td>
<td>173.02</td>
</tr>
<tr>
<td>6</td>
<td>548.15</td>
<td>209.98</td>
</tr>
<tr>
<td>7</td>
<td>583.15</td>
<td>240.97</td>
</tr>
<tr>
<td>8</td>
<td>593.15</td>
<td>249.21</td>
</tr>
<tr>
<td>9</td>
<td>613.15</td>
<td>267.45</td>
</tr>
<tr>
<td>10</td>
<td>644.35</td>
<td>300.34</td>
</tr>
<tr>
<td>Residue</td>
<td>764.83</td>
<td>474.49</td>
</tr>
</tbody>
</table>
The predicted molecular weight are reported in table 5.6. Along with the table 5.6, the predicted molecular weights are plotted against average boiling points of the fractions in figure 5.4. It shows the comparison between the estimated values of molecular weights obtained from different methods. Figure 5.4 showcases the difference between initial values of all methods is small, but the difference has started increasing from 500 K point.

![Graphical presentation of predicted molecular weights](image)

Actually, the estimation of the properties of light hydrocarbons is easier than the heavy hydrocarbons. Most of developed correlations are effective in estimating the properties of light hydrocarbons, but they fail most of time in case of heavy hydrocarbons. The same situation can be observed in figure 5.4. The figure illustrate that the highest prediction of molecular weights estimated by the Riazi-Daubert method; while the lowest prediction generated by the Winn nomogram. The variance discovered between these the predictions depends on various factors such as the applicability range of a method, the data points used during the development of the
method, the theoretical and mathematical approach used in the method, any computational methods that have been employed or not in the development of correlation, etc.

During the development of the prediction method, Goossens (1996) considered the data which obtained from 40 pure hydrocarbons and 23 petroleum fractions in which most of fractions were heavy petroleum fractions. In his analysis, Goossens observed that his correlation had given only 2% of an average error while estimating the molecular weights. Moreover, the predictions obtained from the Goossens correlation in figure 5.4 seems to be appropriate with average molecular weights obtained from all methods employed (in figure 5.4). Therefore, the molecular weights obtained from the Goossens method has been taken as basis to develop the complete molecular weight curve.
The complete molecular weight curve was developed using distribution model developed by Riazi (1989). The molecular weights up to 95% point are predicted and plotted against the cumulative weight percent in figure 5.5. The figure shows that the predicted complete molecular weight curve is in good shape with available molecular weights.
5.4 Kinematic Viscosity

The kinematic viscosities of all petroleum fractions were measured using ASTM D445 (the glass capillary viscometer) and ASTM D2893 (brook field viscometer) described in sections 3.3 and 4.3. The glass capillary viscometers were applied to measure the viscosities of the petroleum fractions (1-10 fractions), where the brook field viscometer was used to measure the viscosity of the residue and the crude oil. As discussed in section 2.2.2.3, it is fairly difficult and complex procedure to predict the kinematic viscosities of the petroleum fraction from the measured properties such as boiling points, specific gravities, API gravities, etc. But still there are variety of prediction methods available by which the viscosities can be predicted with an average error range between 6-20%.

<table>
<thead>
<tr>
<th>Fractions</th>
<th>Tbi, Kelwin</th>
<th>Kinematic Viscosities, cSt</th>
<th>Experimental</th>
<th>Moharam</th>
<th>Twu</th>
<th>Abbott</th>
<th>API-TDB</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>363.15</td>
<td>-</td>
<td>0.6091</td>
<td>0.5146</td>
<td>0.7920</td>
<td>1.1551</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>403.15</td>
<td>0.827</td>
<td>0.7637</td>
<td>0.6883</td>
<td>0.8728</td>
<td>1.2631</td>
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<tr>
<td>3</td>
<td>453.15</td>
<td>1.107</td>
<td>1.0974</td>
<td>1.0489</td>
<td>1.0495</td>
<td>1.5374</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>473.15</td>
<td>1.837</td>
<td>1.2538</td>
<td>1.0317</td>
<td>1.0836</td>
<td>1.5970</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>498.15</td>
<td>2.273</td>
<td>1.8157</td>
<td>1.7385</td>
<td>1.3150</td>
<td>1.9580</td>
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</tr>
<tr>
<td>6</td>
<td>548.15</td>
<td>3.591</td>
<td>3.4755</td>
<td>3.3709</td>
<td>1.7391</td>
<td>2.6483</td>
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</tr>
<tr>
<td>7</td>
<td>583.15</td>
<td>5.951</td>
<td>5.5822</td>
<td>5.6715</td>
<td>2.1552</td>
<td>3.3190</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>593.15</td>
<td>9.321</td>
<td>6.2228</td>
<td>5.8286</td>
<td>2.1908</td>
<td>3.3917</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>613.15</td>
<td>14.665</td>
<td>10.5593</td>
<td>9.8077</td>
<td>2.7208</td>
<td>4.2392</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>644.35</td>
<td>26.780</td>
<td>19.7717</td>
<td>17.9799</td>
<td>3.5073</td>
<td>5.4362</td>
<td></td>
</tr>
<tr>
<td>Residue</td>
<td>764.83</td>
<td>29735</td>
<td>257.3709</td>
<td>259.3839</td>
<td>11.1169</td>
<td>13.0954</td>
<td></td>
</tr>
</tbody>
</table>

The experimental kinematic viscosities and the predicted viscosities from different methods are included in table 5.7. A very small amount fluid was received during the first fraction which was
not sufficient for the experiment of the kinematic viscosity; therefore the experimental value is not reported for fraction in the table 5.7. The four available methods are used for the prediction of kinematic viscosities of the fractions. In the comparison, the experimental viscosities and predicted viscosities are plotted against the average boiling points of fractions in figure 5.6.

The figure shows that the kinematic viscosities increase as the fractions become heavier. The viscosities are increasing with the boiling points of petroleum fractions. From table 5.7 and figure 5.6, one can realize the level of difficulty and complexity present in predicting the kinematic viscosities of petroleum fraction especially for heavy fractions. The two methods namely Moharam and Twu have generated feasible viscosities up to 10th fraction, but they have also failed in predicting the viscosity for the residue. The reason behind this failure is the
presence of more heavy hydrocarbons in the residue. The kinematic viscosity of the residue was measured experimentally and the measured viscosity is around 29735 cSt. It is a way beyond the applicability of all methods used. The Moharam’s method and the Twu method have generated the kinematic viscosities for the residue are around 260 cSt, while the remaining two methods Abbott and API-TDB are not even crossed the experimental value of 9th fraction that is 14.66. Abbott and API-TDB methods have been failed because of their small range of applicability.

The viscosity of residue which had a boiling point of 764 K as shown in Figure 5.6 was found out using Brook field viscometer, while the viscosities of all the other fractions were measured using a standard glass viscometer. It is very clear from the figure that this last value doesn’t follow the same trend as the viscosities of other fractions and thus can be considered as an outlier. The reason of this discrepancy could be due to instrumental error associated with Brook field viscometer.

According to Riazi’s analysis (Riazi, Characterization and properties of petroleum fractions, 2005), he said the heavy oil fraction whose API gravity is less than 10 could have kinematic viscosity of several millions cSt. In short, the prediction of kinematic viscosities of light petroleum fractions are feasible but it is very difficult and complex for the heavy oil or fractions.
5.5 WTI crude oil Assay

As Environment Canada, Emergencies Science and Technology Department (Environment Canada, 1994) published a crude oil assay for WTI, a similar crude assay is developed for WTI crude oil using the results obtained in this project work.

Table 5.8- WTI crude assay developed from the results obtained

<table>
<thead>
<tr>
<th>West Texas Intermediate</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Origin:</td>
<td>Texas and Southern Oklahoma, USA</td>
</tr>
<tr>
<td>API Gravity:</td>
<td>25.98</td>
</tr>
<tr>
<td>Specific Gravity at 60/60°F:</td>
<td>0.8985</td>
</tr>
<tr>
<td>Density (kg/m³):</td>
<td>894.61</td>
</tr>
<tr>
<td>Average Boiling Points (K):</td>
<td>VABP (Volume Average Boiling Point) = 624.42</td>
</tr>
<tr>
<td></td>
<td>WABP (Weight Average Boiling Point) = 631.27</td>
</tr>
<tr>
<td></td>
<td>CABP (Cubic Average Boiling Point) = 608.53</td>
</tr>
<tr>
<td>Kinematic Viscosity at 38°C (100°F) (cSt):</td>
<td>107.35</td>
</tr>
<tr>
<td>Dynamic Viscosity 38°C (100°F) (cP):</td>
<td>120</td>
</tr>
<tr>
<td>Boiling Point distribution (Vol %):</td>
<td>Cum Volume %</td>
</tr>
<tr>
<td>0.53</td>
<td>373.80</td>
</tr>
<tr>
<td>5.33</td>
<td>424.01</td>
</tr>
<tr>
<td>17.28</td>
<td>488.04</td>
</tr>
<tr>
<td>26.67</td>
<td>527.04</td>
</tr>
<tr>
<td>36.78</td>
<td>565.89</td>
</tr>
<tr>
<td>45.06</td>
<td>597.29</td>
</tr>
<tr>
<td>51.22</td>
<td>621.19</td>
</tr>
<tr>
<td>60.42</td>
<td>658.87</td>
</tr>
<tr>
<td>70</td>
<td>702.95</td>
</tr>
<tr>
<td>80</td>
<td>759.30</td>
</tr>
<tr>
<td>90</td>
<td>841.45</td>
</tr>
<tr>
<td>95</td>
<td>912.20</td>
</tr>
<tr>
<td>Molecular Weight Distribution (Weight %):</td>
<td>Cum Weight %</td>
</tr>
<tr>
<td>-----------------------------------------</td>
<td>--------------</td>
</tr>
<tr>
<td></td>
<td>0.47</td>
</tr>
<tr>
<td></td>
<td>4.78</td>
</tr>
<tr>
<td></td>
<td>10.87</td>
</tr>
<tr>
<td></td>
<td>15.96</td>
</tr>
<tr>
<td></td>
<td>25.02</td>
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<td>43.59</td>
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<td>59.69</td>
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<tr>
<td></td>
<td>90.00</td>
</tr>
<tr>
<td></td>
<td>95.00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Yield On Crude (Volume %):</th>
<th>Boiling Point Ranges</th>
<th>Volume %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>°C</td>
<td>K</td>
</tr>
<tr>
<td></td>
<td>0-100</td>
<td>273.15-373.15</td>
</tr>
<tr>
<td></td>
<td>100-160</td>
<td>373.15-433.15</td>
</tr>
<tr>
<td></td>
<td>160-200</td>
<td>433.15-473.15</td>
</tr>
<tr>
<td></td>
<td>0-200</td>
<td>273.15-473.15</td>
</tr>
<tr>
<td></td>
<td>200-250</td>
<td>473.15-523.15</td>
</tr>
<tr>
<td></td>
<td>250-300</td>
<td>523.15-573.15</td>
</tr>
<tr>
<td></td>
<td>300-320</td>
<td>573.15-593.15</td>
</tr>
<tr>
<td></td>
<td>0-320</td>
<td>273.15-593.15</td>
</tr>
<tr>
<td></td>
<td>320-360</td>
<td>593.15-633.15</td>
</tr>
<tr>
<td></td>
<td>360-382.4</td>
<td>633.15-655.55</td>
</tr>
<tr>
<td></td>
<td>382.4&lt;</td>
<td>655.15&lt;</td>
</tr>
</tbody>
</table>
6 CONCLUSION

The following conclusions are made based on the results obtained during the experimental analysis:

1. The true boiling point curve for West Texas Intermediate crude oil has been developed successfully using ASTM D2892 test method.

2. Specific gravity measurements of all petroleum fractions and the crude oil were made using the hydrometer technique described in ASTM D1298. From these specific gravity measurements, the densities at 20°C were predicted and the density curve have been developed successfully for the crude oil.

3. Molecular weights of all petroleum fractions were estimated using several prediction correlations available. Among the different correlations used, Goossens method and Twu methods appeared to yield appropriate estimations of the molecular weights. Based on the best predictions obtained, the molecular weight curve has been constructed well for the crude oil.

4. The glass capillary viscometer and brook field viscometer have been used successfully for the measurements of kinematic viscosities of petroleum fractions and the crude oil. The accurate viscosity measurements are feasible for light petroleum fractions, but it is very challenging for heavy fractions or oils.

5. A variety of kinematic viscosity prediction correlations are available, but still the accurate viscosity estimation is not possible for the heavy hydrocarbon fraction. It is impossible to predict the viscosities of heavy hydrocarbons. Among the correlations used for predictions of kinematic viscosities, Moharam’s method and Twu’s method have estimated the viscosities well up to 20 cSt.
6. The true boiling point curve, density curve, and molecular weight curve have been extended successfully for the crude oil by using Riazi’s distribution model. All curves have drawn up to 95% of volume vaporized.
7 SUGGESTIONS FOR FUTURE WORK

Although the main areas of the characterization of WTI have covered in this project work, it could be further developed in number of ways:

1. The molecular weights curve of WTI has developed here based on the predicted values of molecular weights, but one can determine the actual molecular weight distribution throughout the crude oil using a gas chromatography.

2. Various properties such as surface tension, aniline point, flash point, pour point, CH ratio, composition distribution of hydrocarbon, etc. have not included in this work. Therefore, another way would be to measure these remaining properties in order to complete the characterization of the crude oil.

3. By using the experimental data from this project work, the complete characterization of WTI crude oil could be done in simulation softwares such as Aspen plus, Hysys, or Unisim.

4. There is lack of quality correlations available for predicting kinematic viscosities of heavy hydrocarbons, so one can take challenge to develop a better correlation for the kinematic viscosity using minimum input parameters.

5. For design and simulation of any distillation column for crude oil, it requires a basic data of true boiling point curve, density curve, molecular curve, and kinematic viscosity curve. So that, one can design a distillation tower for refining WTI crude oil using the results presented in this project work.
REFERENCES


IUPAC, the International Union of Pure and Applied Chemistry. (May 2013.). IUPAC Periodic Table of the Elements.


