Generalized Equation for Thermophysical Properties

Riazi and Al-Sahhaf (1996) presented a method for the calculation of different properties such as the NBP, density, refractive index, critical temperature, pressure and density, acentric factor, solubility parameter and surface tension given only the molecular weight and using the following general equation

\[ \theta = \theta_\infty - \exp(a - bM^c) \]  

where \( \theta \) can be any one of the properties mentioned above. \( M \) is the molecular weight and \( \theta_\infty \) is the limiting value for any property as \( M \to \infty \). This generalized equation can be used to calculate the following properties knowing the molecular weight.

- \( T_b \), the mean average boiling point, K
- \( SG \), the specific gravity
- \( d_{20} \), the liquid density at 20 °C or 68 °F
- \( I \), the Huang characterization parameter
- \( T_{br} = T_b/T_c \), the reduced boiling point which is used to calculate the critical temperature in K
- \( P_c \), the critical pressure in bars
- \( d_c \), the critical density in g/cm³
- \( \omega \), the acentric factor
- \( \sigma \), the surface tension in dynes/cm
- \( \delta \), the solubility parameter, in (cal/cm³)²

The constants \( a, b \) and \( c \) for each property are given in Table 3.6.

The application of this correlation is simple. You only need to know the average NBP of the petroleum fraction. First, the molecular weight is calculated from the correlation using the constants for the boiling point. Once the molecular weight is known, other properties can be calculated using equation \( A^* \) with the appropriate constants from Table 3.6.

### Table 3.6 Constants for the Riazi–Al-Sahhaf equation

<table>
<thead>
<tr>
<th>( \Theta )</th>
<th>( \theta_\infty )</th>
<th>( a )</th>
<th>( b )</th>
<th>( c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_b )</td>
<td>1080</td>
<td>6.97996</td>
<td>0.01964</td>
<td>0.67</td>
</tr>
<tr>
<td>( SG )</td>
<td>1.07</td>
<td>3.56073</td>
<td>2.93886</td>
<td>0.1</td>
</tr>
<tr>
<td>( d_{20} )</td>
<td>1.05</td>
<td>3.80258</td>
<td>3.12287</td>
<td>0.1</td>
</tr>
<tr>
<td>( I )</td>
<td>0.34</td>
<td>2.30884</td>
<td>2.96508</td>
<td>0.1</td>
</tr>
<tr>
<td>( T_{br} )</td>
<td>1.20</td>
<td>-0.34742</td>
<td>0.02327</td>
<td>0.55</td>
</tr>
<tr>
<td>( -P_c )</td>
<td>0</td>
<td>6.34492</td>
<td>0.72390</td>
<td>0.3</td>
</tr>
<tr>
<td>( -d_c )</td>
<td>-0.22</td>
<td>-3.2201</td>
<td>0.00090</td>
<td>1</td>
</tr>
<tr>
<td>( -\omega )</td>
<td>0.30</td>
<td>-6.2520</td>
<td>-3.64457</td>
<td>0.1</td>
</tr>
<tr>
<td>( \Sigma )</td>
<td>30.3</td>
<td>17.45018</td>
<td>9.70188</td>
<td>0.1</td>
</tr>
<tr>
<td>( A )</td>
<td>8.60</td>
<td>2.29195</td>
<td>0.54907</td>
<td>0.3</td>
</tr>
</tbody>
</table>
Crude Oil Pre-treatment (desalting)

When the crude oil enters the unit, it carries with it some brine in the form of very fine water droplets emulsified in the crude oil. The salt content of the crude measured in pounds per thousand barrels (PTB) can be as high as 2000. Desalting of crude oil is an essential part of the refinery operation. The salt content should be lowered to between 5.7 and 14.3 kg/1000m$^3$ (2 and 5 PTB). Poor desalting has the following effects:

- Salts deposit inside the tubes of furnaces and on the tube bundles of heat exchangers creating fouling, thus reducing the heat transfer efficiency;
- Corrosion of overhead equipment; and,
- The salts carried with the products act as catalyst poisons in catalytic cracking units.

The two most typical methods of crude-oil desalting, chemical and electrostatic separation, use hot water as the extraction agent. In chemical desalting, water and chemical surfactant (demulsifiers) are added to the crude, heated so that salts and other impurities dissolve into the water or attach to the water, and then held in a tank where they settle out. Electrical desalting is the application of high-voltage electrostatic charges to concentrate suspended water globules in the bottom of the settling tank. Surfactants are added only when the crude has a large amount of suspended solids. Both methods of desalting are continuous. A third and less-common process involves filtering heated crude using diatomaceous earth.

In both methods, the feedstock crude oil is heated to between 150° and 350°F to reduce viscosity and surface tension for easier mixing and separation of the water. The temperature is limited by the vapor pressure of the crude-oil feedstock. In both methods other chemicals may be added. Ammonia is often used to reduce corrosion. Caustic or acid may be added to adjust the pH of the water wash. Wastewater and contaminants are discharged from the bottom of the settling tank to the wastewater treatment facility. The desalted crude is continuously drawn from the top of the settling tanks and sent to the crude distillation (fractionating) tower.
Fractionation of Crude Oil

1- Atmospheric Distillation
Crude distillation unit (CDU) is at the front-end of the refinery, also known as topping unit, or atmospheric distillation unit. It receives high flow rates hence its size and operating cost are the largest in the refinery. The capacity of the CDU ranges from 10,000 barrels per stream day (BPSD) or 1400 metric tons per day (tpd) to 400,000 BPSD (56,000 metric tpd). The economics of refining favours larger units. A good size CDU can process about 200,000 BPSD.

These towers can be up to 150 feet (50 meters) high and contain 20 to 40 fractionation trays spaced at regular intervals. Before entering the column distillation, desalted crude oil pass through a network of pre-heat exchangers in order to heat it initially with hot material drawn from the bottom of the distillation tower to raise its temperature up to 450°F and then to a heating furnace, which brings the temperature up to about 650°F. This part of process is essential because the carbon will be deposited inside the pipes and equipment through which it flows when the oil gets much hotter. The hot crude oil enters the column distillation and most of it vaporizes. Unvaporized heavy oil cuts and residue will drop to the bottom of the column, where it is drawn off. Inside the tower distillation column, there are the so-called trays (Figure 22 below), which are working mainly in the separation of crude oil to light the required derivatives. These trays permit the vapors from below to pass from it and contact with the condensed liquid on top of the tray that provides excellent contact between vapor and liquid. Condensed liquid flows down through a pipe to the hotter tray below, where the higher temperature causes re-evaporation. A given molecule evaporates and condenses many times before finally leaving the tower.

Products are collected from the top, bottom and side of the column. Side draw products are taken from trays at which the temperature corresponds to the cut point for a desired product. In modern towers, a portion of each side draw stream is returned to the tower to control tray temperatures and further enhance separation. Part of the top product is also returned; this “reflux” plays a major role in controlling temperature at the top of the tower.

Figure 22: Distillation column with trays
Fractionation process depends on
1- Number of Trays
2- Reflux ratio
3- Quantity of steam added to the column

As increasing in trays no. and reflux ratio, the efficiency of separation process is increasing. Typical designs have the trays distribution between products as shown in Table below.

<table>
<thead>
<tr>
<th>Zone</th>
<th>Number of trays</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overhead product to kerosene</td>
<td>10</td>
</tr>
<tr>
<td>Kerosene to light gas oil</td>
<td>8</td>
</tr>
<tr>
<td>Light gas oil to heavy gas oil</td>
<td>6</td>
</tr>
<tr>
<td>Heavy gas oil to flash zone</td>
<td>6</td>
</tr>
<tr>
<td>Flash zone to atmospheric residue</td>
<td>6</td>
</tr>
<tr>
<td>Pumparounds</td>
<td>3–4</td>
</tr>
</tbody>
</table>

The degree of separation process inside the distillation column depends on

1- **Degree of difficulty of separation** (represents the difference between $T_{50\%}$ for two consecutive cuts, i.e., an increasing in $T_{50\%}$ means that the range of the cut becomes wide and easy to separate). On the other hand, needs low reflux ratio and less no. of trays.

2- **Degree of separation** (is called ASTM Gab, which is represents the difference between $T_{5\%}$ and $T_{95\%}$ for two consecutive cuts). Whenever a big difference, separation between to cuts becomes small and as a result required more trays and high reflux ratio.

**Operation of Crude Distillation Units**

In this section, the factors which affect the design and operation of the unit are explored.

1) **Fractionation** or separation (mentioned above)

2) **Cut Points**: The cut points in the CDU are controlled by the overhead vapour temperature which determines how much vapour goes to the condensers to produce light naphtha and by the flow rate of the various products straight from the column or the side stream strippers. The atmospheric residue level control inside the column determines its flow rate and thus its initial cut point. The amount of light naphtha is determined by the dew point of the naphtha at its partial pressure, which is close to the overhead temperature.

3) **Overflash**: In order to fractionate the crude oil into the various products, it has to be heated to a temperature between 330 and 385 °C (626 and 725 °F), depending
on the crude composition. The partially vaporized crude is transferred to the flash zone of the column located at a point lower down the column. The furnace outlet temperature should be enough to vaporize all products withdrawn above the flash zone plus about 3–5 vol% of the bottom product. This overflash has the function of providing liquid wash to the vapors going up the column from the flash zone, and improving fractionation on the trays above the flash zone, thereby improving the quality of the HGO and reducing the overlap with the bottom products below the flash zone.

4) **Column Pressure**: The pressure inside the CDU column is controlled by the back pressure of the overhead reflux drum at about 0.2–0.34 bar gauge (3–5 psig). The top tray pressure is 0.4–0.7 bar gauge (6–10 psig) higher than the reflux drum. The flash zone pressure is usually 0.34–0.54 bar (5–8 psi) higher than the top tray.

5) **Overhead Temperature**: The overhead temperature must be controlled to be 14–17 °C (25–31 °F) higher than the dew point temperature for the water at the column overhead pressure so that no liquid water is condensed in the column. This is to prevent corrosion due to the hydrogen chloride dissolved in liquid water (hydrochloric acid).

**Example**

If the overhead stream contains 8.5 mol% water at a pressure of 34.7 psia (2.36 bars), calculate the overhead temperature for safe operation.

**Solution:**

The saturation temperature of water at the partial pressure of water in the overhead vapour.

Water partial pressure = 0.085 × 2.36 = 0.2 bars

From the steam tables:

Saturated steam temperature at 0.2 bars = 61 °C

Safe overhead operating temperature = 61 + 17 = 78 °C

6) **Pre-flash Columns and Crude Column Capacity**: The crude flow rate to the CDU determines the capacity of the whole refinery. A crude column is typically designed for 80% loading, which means that the unit can be operated at 20% throughput more than the design value. The capacity of the column is limited by the vapour flow rate with a velocity between 2.5 and 3.5 ft/s (0.76 and 1.07 m/s). The vapour flow rate increases as the vapours rise from the flash zone to the overhead.