A.P.I. Gravity

A special scale has been developed by the American Petroleum Institute (A.P.I.) which is now used by the petroleum industry to determine the gravity of petroleum products. This scale extends in practical use from 0, which would represent a very heavy petroleum tar, to about 75, which would represent an exceedingly light naphtha. The numbers in the A.P.I. scale are called degrees and are identified by the symbol "°A.P.I." Thus, cracking coil tar with a specific gravity of 1.00 is known as 10° A.P.I. tar on the A.P.I. scale. All A.P.I. gravity values represent the gravity of the product when it is at 60°F. Although A.P.I. hydrometers may be used at temperatures other than 60°F, tables must be used to convert the observed value to the value which it would have at 60°F. The "Tag Manual for Petroleum Inspectors" has the conversion tables required.

Pressure due to Liquids

A liquid exerts pressure on the sides and bottom of a containing vessel, depending on the depth of the liquid and its density. If a pressure gauge is attached to the side of a tank of water at 68°F, at the surface of the water, the gauge would register 0 pounds per square inch gauge. At a depth of 1 foot it would register 0.433 pounds per square inch gauge (62.38 pounds per square foot gauge). For each additional foot of depth, the gauge would show an increase of 0.433 pounds per square inch gauge. At a depth of 33.93 feet (equivalent to 29.92 inches of mercury = atmospheric pressure) the gauge would show a pressure of 14.7 pounds per square inch gauge (or 2116.8 pounds per square foot gauge).

If a liquid heavier than water, or water colder than 68°F, were in the tank, the pressure created would be greater. Conversely, if the liquid were lighter than water or were water warmer than 68°F, the pressures would be less.

The fact that liquid pressure is due to its depth leads to an unexpected answer to this problem:

Tanks (a) and (b), in diagram A on page 10, are both full to the top with water. Tank (a) has a 10 foot by 10 foot bottom and is 10 feet high. It contains 62,380 pounds of water. Tank (b) has a 10 foot by 10 foot bottom also, but contains only 6,862 pounds of water, since the upper 9 feet of the 10 foot total height has been reduced to only 1 square foot in cross section (one foot to a side). What is the total pressure on the bottom of each tank?

Answer: The pressure on both bottoms is the same. Both bottoms have 100 square feet and the total depth of each tank is 10 feet. Thus, 100 x 10 x 62.38 = 62,380 pounds pressure as the total pressure on each bottom, despite the fact that there are only 6,862 pounds altogether in Tank (b).

If a tank with a vertical pipe running from the top of it fills, the pressure on the bottom of the tank will increase rapidly as the pipe fills.

The distance between the upper surface of a liquid and any point below the surface where the pressure is measured is called the "pressure head" or simply the "head". Thus, the pressure at the bottom of a tank of water is
spoken of as a head of so many feet of water. (Each foot equal to about 62.38 pounds gauge per square foot or 0.433 pounds gauge per square inch). If the tank contained kerosene, the head would be so many feet of kerosene (each foot equal to about 50 pounds gauge per square foot or 0.347 pounds gauge per square inch).

Other Definitions concerning Liquids at Rest.

1. The free or upper surface of a liquid at rest is always horizontal.

2. The surfaces of a liquid in a series of tanks, stills or other vessels, which are connected by pipes through which the liquid can flow, will always be at the same level. This is illustrated by diagram B, page 10.

3. If two liquids of different specific gravity that do not mix together, such as oil and water, are in a system of connected vessels, as shown in B, page 10, the level in each vessel will also depend on the specific gravity of the liquid present. Since oil is lighter than water, a greater height of oil is required to balance the water. This is illustrated in diagram C, page 10.

4. Archimedes principle: An object wholly or partially immersed in a liquid experiences an apparent loss of weight, which is exactly equal to the weight of the liquid displaced.

Liquids in Motion

The motion of liquids (or gases) may be steady or unsteady. In steady motion each particle of liquid travels in exactly the same path as the particle ahead of it, thus setting up streamline lines which may be straight or curved. This is called "streamline flow". In unsteady motion the particles tend to scatter, thus setting up eddies. This is called "turbulent flow". A slow-moving stream is usually streamline. As the rate of flow increases streamline flow is maintained until a certain critical velocity is reached above which turbulent flow sets in.

Turbulent flow is the condition in most of the lines and pipes in the refinery. This is due to the fact that the number of gallons of liquid that can be delivered per minute is greater under the high velocity turbulent flow condition than under the low velocity streamline flow condition. The high velocity is obtained only by use of high pressures, which requires a greater consumption of power by the pumps concerned. In addition to high stream velocity, roughness inside the pipe, abrupt changes in diameter or direction of the pipe also cause turbulence. Turbulence is particularly desirable in the tubes of tube still furnaces, heat exchangers, and in mixers.

Flow takes place through a pipe due to pressure created by the head of liquid, or due to a pump. Thus, the liquid on entering a pipe is under a certain pressure. As the liquid moves down the pipe internal friction within the liquid (which is quite high in case of turbulent flow), friction between the liquid and the wall of the pipe (which can also be high if the pipe is rough or corroded), constrictions in the pipe, elbows, tees, etc., all cause losses in pressure. This loss in pressure is called "loss in head" or "pressure drop".
HEAT AND LIQUIDS

When heat is applied to a liquid, its molecules vibrate faster. This faster vibration causes the liquid to expand slightly and the temperature of the liquid to rise. The expansion and temperature rise continues until the vapor pressure of the liquid equals the pressure of the atmosphere. Vapor pressure, as described before, is due to the faster molecules escaping from the liquid into the vapor space above. As the temperature rises, more faster molecules are created, thus the vapor pressure increases. Vapor pressure is dependent only on the temperature. At the boiling temperature great numbers of molecules throughout the liquid have sufficient velocity to escape together from the liquid. This is indicated by the formation of bubbles of vapor within the liquid. This is boiling. Each liquid has its own definite boiling temperature, usually referred to as the boiling point. This boiling point is so characteristic of the different liquids that it is frequently used as a means of identifying an unknown liquid.

Since the temperature at which a liquid boils is dependent on the pressure which exists on the liquid, boiling points are expressed as so many degrees Fahrenheit at a certain pressure. The usual pressure is the pressure of the atmosphere. The pressure of the atmosphere, however, varies slightly, so a standard atmospheric pressure of 14.7 pounds per square inch is used. The boiling points of several substances at standard atmospheric pressure are as follows:

<table>
<thead>
<tr>
<th>Substance</th>
<th>Boiling Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>212°F.</td>
</tr>
<tr>
<td>Alcohol</td>
<td>172.4</td>
</tr>
<tr>
<td>Glycerine</td>
<td>554</td>
</tr>
<tr>
<td>Mercury</td>
<td>675</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>-423</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>-320</td>
</tr>
</tbody>
</table>

The table "Properties of Hydrocarbons" in Section 2 gives the boiling point of various hydrocarbons.

Effect of Pressure and Vacuum on Boiling Point

As pointed out above, the boiling point is dependent on the pressure. In other words, the temperature at which bubbles of vapor will form in a liquid is dependent on the external pressure applied to the liquid. This follows from the fact that boiling takes place when the vapor pressure of the liquid equals that of the external pressure, which is usually that due to the atmosphere. If the external pressure is removed, boiling would be expected to occur at lower temperatures. This does occur. For example, water will boil at room temperature if the air is pumped out from above the liquid. In the petroleum industry, boiling under reduced pressures or vacuum is very important. Distillation depends on converting petroleum liquids to petroleum vapors. Many hydrocarbons in lubricating oils require temperatures of 1000 or higher at standard atmospheric pressure, in order to go from the liquid to the vapor state. Such temperatures, however, decompose or crack the lubricating oil hydrocarbons into small molecules with none of the properties of lubricating oil. Consequently, distillation of lubricating oils cannot be carried out at atmospheric pressure. By reducing the pressure in the stills by means of radojets, these hydrocarbons can be converted from the liquid to the vapor state (i.e., made to boil) at temperatures several hundred degrees lower, where cracking does not take place.
If pressures greater than atmospheric pressure are imposed on a liquid, the liquid will not boil until a temperature higher than normal is reached. In steam boilers, pressures of hundreds of pounds are maintained. Water under 250 pounds pressure per square inch will not boil until a temperature of 401°F. is reached.

To separate gaseous hydrocarbons from one another by fractional distillation it is necessary that the gases be liquefied. This could be done by chilling the gases to very low temperatures (methane, for example, would have to be chilled to 258.5°F. below zero before it would condense). By boiling at these low temperatures, the gases could be separated by fractional distillation (this is actually done in a laboratory method of analyzing mixtures of hydrocarbon gases known as Podbielniak Distillation). On a plant scale refrigeration to these low temperatures would be prohibitively costly. Consequently boiling takes place at a much higher temperature (about 0°F.) by subjecting the liquefied gases to pressures of the order of 500 pounds per square inch. This will be done in the demethanizer tower of Light Ends Recovery Unit.

Effect of Steam on the Vapor Pressure of a Liquid

If steam (or any other gas) is passed through the space above a liquid, it sweeps out the vapor molecules that have escaped from the liquid almost as fast as they leave the liquid. In effect, the steam causes a partial vacuum as far as the liquid is concerned. This partial vacuum causes the liquid to boil at a lower temperature than normal. Steam is thus added to stills concerned in the fractionation of lubricating oils and other stocks (i.e. naphtha specialties) where the lowest possible distillation temperature is required. In this way, boiling takes place at lower temperatures than would occur if steam were not present.

It should be emphasized that the purpose of the added steam, usually called "open steam", is not to increase the temperature in the still, but to cause the still contents to boil at a lower temperature. Open steam is added below the surface of the liquid to cause stirring. Occasionally, the open steam actually cools hot liquids rather than heats them up.

"Steam distillation" refers to the use of open steam as described above in the separation of fractions. For example, the naphtha is steam distilled from the naphtha-cylinder stock mixture processed in the centrifuge plant to remove petrodatum from the cylinder stock. "Steam stripping" refers to the removal of small amounts of a light product from a heavier fraction. For example, traces of naphtha are steam stripped from kerosene to raise the flash point of the kerosene.

Specific Heat.

If the same number of B.T.U's of heat are added to equal weights of several different substances, a different temperature rise will take place in each substance. In other words, the amount of heat required to raise the temperature of one pound of each substance 1°F. depends on the substance. Thus 1 B.T.U. raises the temperature of 1 pound of water 1°F. Only 0.03 of a B.T.U. is required to raise 1 pound of mercury 1°F. The amount of heat required to raise 1 pound of substance 1°F. is known as the "specific heat" of the substance.
The specific heats of petroleum fractions vary, depending on the gravity of the fraction and the temperature. For example, it takes 0.425 B.T.U. to raise the temperature of a 10° A.P.I. tar from 75 to 76°F and 0.55 B.T.U. to raise its temperature from 400 to 401°F. A 60° A.P.I. naphtha requires about 0.58 B.T.U. to raise its temperature from 75 to 76°F and about 6.75 B.T.U. to go from 400 to 401°F.

Latent Heat

While boiling goes on it will be noted that the temperature does not change despite the fact that large quantities of heat are still being added to the liquid. Why doesn't the temperature rise?

The temperature does not rise because the heat added is all used up in giving the molecules sufficient energy to break from the liquid state into the gaseous state. The amount of heat energy necessary to do this is relatively very large. For example, it takes only 1 B.T.U. to raise the temperature of 1 pound of water 1°F, but it takes 970 B.T.U's to change 1 pound of water at the boiling point to steam. This is shown in the graph on page 14. The heat required to raise the temperature of a liquid or gas is called "sensible heat." This is heat which shows up on the thermometer. The heat required to change liquid into vapor is not so apparent. This is sometimes called "hidden heat." The usual name is "latent heat."

The idea of latent heat is of great importance to the refinery operator, since it is necessary in understanding fractional distillation, vapor heat exchangers, etc. The latent heat which causes the change from the liquid to the vapor state is stored by the vaporized or gaseous molecules. This heat can thus be transported to a place where it is required and then be recovered by simply changing the vapor to a liquid (condensation). When 1 pound of steam is condensed to water at the same temperature (212°F) 970 B.T.U's of heat are given up. This is illustrated on the diagram on page 14. This diagram illustrates how heat is added to a distillation tower by means of a reboiler. Liquid naphtha is shown in the bottom of the tower at 200°F. This naphtha has not enough heat energy to cause it to boil. It is pumped from the bottom of the distillation tower into the reboiler. Steam at 212°F passing through a coil immersed in the naphtha is condensed to water. As each pound of steam condenses 970 B.T.U's of heat are given up to the naphtha. Despite giving up this heat the water leaving the coil is still at 212°F. The latent heat released by the change of state from steam to water causes the liquid naphtha to boil, or in other words, to change from the liquid to the vapor state. The naphtha, as a vapor, is returned to the distillation tower with sufficient energy to permit fractional distillation to take place in the upper part of the tower. It will be noted that large quantities of heat have been exchanged between the steam and the naphtha, without a change in temperature in either of them. In actual refinery operations, of course, use is also made of the sensible heat, which would cause changes in the temperature. This example is designed to emphasize the important fact that heat can be exchanged without temperature changes. This fact will be required in understanding the operation of a fractional distillation tower, to be described later.
Each substance has its characteristic latent heat; that is, one substance requires more heat than another to convert one pound of it from the liquid state to the vapor state. As mentioned above, it takes 970 B.T.U's to convert one pound of water at 212° to steam at the same temperature. Hydrocarbons, in general, require only 140 to 245 B.T.U's to convert one pound of liquid hydrocarbon at its boiling point to vapor at the same temperature. The usual B.T.U. values for latent heats are those associated with boiling points at standard atmospheric pressure. The latent heat B.T.U. value decreases slightly as the boiling temperature is raised by increased external pressure.

**Vapor Pressure of Solutions**

When salt is dissolved in water, a solution is formed. If the vapor pressure of a salt solution is compared with that of water at the same temperature, the vapor pressure of the salt solution will be found lower. This will be found to hold true at all temperatures up to and including the boiling point. Consequently, while water will boil at 212°F., a salt solution at 212° F., has not sufficient vapor pressure to boil. It thus has a higher boiling point. The more salt added, the higher the boiling point is raised. The same is true for any solid or non-volatile liquid that will dissolve in water or any other solvent.

The molecular theory explains this lowering of the vapor pressure (and raising of the boiling point) due to the presence of a dissolved substance, as follows: In a pure liquid (no dissolved substance) every molecule on the surface has an equal chance to escape and thus create vapor pressure. However, if non-volatile molecules are present (such as salt in a salt solution) the number of volatile liquid molecules at the surface of the solution must be reduced. If one in every ten molecules at the surface is salt, then the intensity of the hail of molecules leaving the surface must be reduced by one-tenth. This causes a corresponding decrease in the vapor pressure.

**Expansion of Liquids**

As heat is added to liquids, they expand different amounts, depending on the liquid. Expansion of liquids is expressed as the fraction of the bulk of the liquid that the liquid expands when heated 1° F. This is called the Coefficient of Cubical Expansion. It is three times the Linear Coefficient used to express the lengthening of metal tubes and rods described before. Examples of the cubical expansion of liquids follow.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycerine</td>
<td>.000534</td>
</tr>
<tr>
<td>Phenol</td>
<td>.000899</td>
</tr>
<tr>
<td>Naphtha</td>
<td>.001039</td>
</tr>
<tr>
<td>Sulphuric Acid</td>
<td>.000489</td>
</tr>
</tbody>
</table>

Water changes volume with temperature in an unusual manner. On cooling water down to 39°F, it contracts in the expected manner. From 39°F. to 32°F., however, water expands. On freezing, water expands still more, so that the ice takes up about one-tenth more space than the water. Care must be taken that vessels, pipes, etc., do not freeze, otherwise the pressure created will burst them.

Since liquids are not compressible, expanding liquids can create great pressures. Care should be taken that drums, cans, bottles, etc., should be filled with sufficient space left to allow for expansion.
GASES

When each molecule in a substance leads an individual existence; that is, no attractive force exists between the molecules, the substance is a gas. A "gas" is the same as a "vapor", except that vapor implies that it has been formed by the evaporation of a liquid.

Atmosphere

Air is so common that it is rarely thought of as being a gas, or even as having weight and volume, yet a bottle or a barrel cannot be filled with a liquid unless the air is allowed to get out. If a bottle full of air is weighed and then the air pumped out and the bottle weighed again, it will be found that air has weight. One cubic foot of air weighs about 1.2 ounces or 0.075 pounds. Therefore, the density of air is 0.075 and its specific gravity is 0.0012. Changes in atmospheric pressure and varying amounts of moisture will change the above density and specific gravity figures.

Air which consists of approximately 77.1 percent by volume of nitrogen, 20.8 percent oxygen, 1.2 percent moisture, 0.9 percent argon, and traces of carbon dioxide, neon, xenon and krypton, forms the atmosphere. This atmosphere rests on the surface of the earth, just as a body of water rests on the bottom of a lake. Consequently, the atmosphere exerts pressure on the earth's surface. This pressure, however, is not constant since winds and the heat of the sun change the density and the distribution of the atmosphere over the earth's surface. Since a standard atmospheric pressure is desirable, the value of 14.7 pounds gauge per square inch has been selected as the average figure of atmospheric pressure at sea level.

The pressure of the atmosphere is measured by means of the barometer. This is essentially a glass tube containing mercury and so arranged that the pressure of the atmosphere is balanced against the pressure exerted by the weight of the mercury in the tube. At sea level the atmosphere will balance a column of mercury 29.92 inches high (76 centimeters). If water were used in the tube, the tube would have to be 33.9 feet high. Atmospheric pressure is recorded as the height of mercury in the barometer in inches or centimeters.

Atmospheric pressure varies from hour to hour in any locality. In Sarnia, the atmospheric pressure ranges between 28.55 inches (72.5 cm) and 29.73 inches (75.5 cm) and averages about 29.14 inches (74.0 cm). Atmospheric pressure decreases with the distance above sea level, since the air thins out (decreases in density) the higher it is. Three and a half miles up the atmospheric pressure is only about one-half that at sea level. At an altitude of seven miles the pressure is only one-fifth the pressure at atmospheric level. At such altitudes, where the pressure is about 2 pounds per square inch, gasoline used in aircraft would change in part to vapor in the fuel lines, (vapor lock) if its Reid Vapor Pressure was too high. Consequently aviation gasoline has a maximum specification of 7 pounds R.V.P.

Gauge and Absolute Pressure

Since the atmosphere is always present, it is frequently forgotten that it exerts a pressure. The water in a tank, for example, is said to exert so many pounds pressure per square inch on the bottom of the tank. The pressure referred to is due to the weight of the water present. The fact that the atmosphere is pressing down on top of the water is not considered, although this, of course, is actually the case. The reason that it is frequently forgotten is because the atmosphere extends underneath the tank, creating an upward pressure
which balances the downward pressure of the air. In certain instances, however, the effect of the atmosphere must be considered. For example, atmospheric pressure becomes an important factor in the designing of vacuum equipment.

Gauges are used to measure pressure. Most gauges are set to read zero when open to the atmosphere. Actually the pressure on the gauge is the atmospheric pressure of 14.7 pounds per square inch. Such gauges, therefore, measure only increases in pressure above atmospheric pressure. Readings from such a gauge are expressed as so many pounds per square inch "gauge". Other gauges are set to read zero in a complete vacuum and consequently read 14.7 pounds when open to the atmosphere. Readings on these gauges are expressed as so many pounds per square inch "absolute". The following table shows the relationship between gauge readings, absolute readings, inches of mercury pressure and inches of mercury vacuum. The inches of mercury refer to the height of a column of mercury that counter-balances the pressure or vacuum under consideration.

<table>
<thead>
<tr>
<th>PRESSURE SCALES</th>
</tr>
</thead>
<tbody>
<tr>
<td>GAUGE SCALE</td>
</tr>
<tr>
<td>Pounds per</td>
</tr>
<tr>
<td>Square Inch.</td>
</tr>
<tr>
<td>Inches of</td>
</tr>
<tr>
<td>Mercury.</td>
</tr>
<tr>
<td>30</td>
</tr>
<tr>
<td>25</td>
</tr>
<tr>
<td>20</td>
</tr>
<tr>
<td>15</td>
</tr>
<tr>
<td>10</td>
</tr>
<tr>
<td>5</td>
</tr>
<tr>
<td>Atmospheric</td>
</tr>
<tr>
<td>Pressure-0</td>
</tr>
<tr>
<td>5</td>
</tr>
<tr>
<td>10</td>
</tr>
<tr>
<td>Complete</td>
</tr>
<tr>
<td>Vacuum</td>
</tr>
</tbody>
</table>

The line representing complete vacuum never varies. This is the point at which no pressure exists. In practice, this point is never reached since a small amount of residual pressure always remains.

Gauge pressure is pressure above atmospheric. Since atmospheric pressure varies with height above sea level, the gauges must be set for zero reading at atmospheric pressure in each locality. The gauge scale starts at atmospheric pressure and goes up. The vacuum scale starts at atmospheric pressure and goes down. Absolute starts at complete vacuum and goes up.
THE GAS LAWS

All gases behave in almost the same manner, when subjected to the same conditions. The statement describing the behaviour of gases under various conditions of temperature, pressure etc., are called the Gas Laws. By these laws the effect on a gas of changing temperature, changing pressure and changing volume can be calculated.

Fundamental Gas Law \((PV = RT)\)

This law summarizes the effect of temperature, pressure and volume on a gas. It is developed from two other laws, as follows:

Boyle's Law: The volume of a gas varies inversely with the pressure, if the temperature remains constant.

As a piston moves into a cylinder, the gas is crowded into a smaller space. As the volume of the gas is decreased, the pressure on the gas is increased in proportion. If the volume is reduced to one-half, the pressure is doubled. When the volume is one-half, the gas molecules have only half the distance to go to reach a wall. Consequently, they hit the walls twice as often and thus double the pressure. The relationship between volume \((V)\) and pressure \((P)\) of a gas at constant temperature may be expressed as follows:

\[ V \text{ is proportional to } \frac{1}{P} \text{ (Temperature fixed)} \]

Gay - Lussac's Law describes the variation of volume with temperature. It states that the volume of a gas is directly proportional to its absolute temperature, if the pressure remains constant. This may be expressed as follows:

\[ V \text{ is proportional to } T \text{ (Pressure fixed)} \]

The "absolute temperature" \((T)\) is the number of degrees above "absolute zero", the temperature at which molecules lose all movement. Since heat causes molecules to move, absolute zero is the temperature at which molecules "have no heat". This temperature is the same for all substances. On the Fahrenheit scale, this temperature is \(-459.66\)°F. Thus the absolute temperature is the temperature as read on an ordinary Fahrenheit thermometer plus 459.6.

Boyle's and Gay - Lussac's laws are combined, as follows:

\[ V \text{ is proportional to } \frac{T}{P} \]

The volume \((V)\) is made equal to the result obtained by dividing the absolute temperature by the pressure \((T/P)\) by multiplying the latter by a constant quantity \((R)\). Thus:

\[ V = R \frac{T}{P} \text{ which can be transposed to} \]

\[ VP = RT \]
The value of "R" depends on the amount of gas concerned and the units in which the volume and pressure are expressed. If it is desired, for example, to find what volume a gas would occupy when its temperature and pressure changes, the "R" disappears, as follows:

\[ V_1 \frac{P_1}{T_1} = \frac{V_2}{T_2} \]

\[ V_1 \frac{P_1}{T_1} = V_2 \frac{P_2}{T_2} \]

V\(_1\) represents the relations between the volume, pressure and temperature at one set of conditions.

V\(_2\) represents the relationship for the same gas at a new set of values for the volume, pressure and temperature.

If one expression is divided by the other, the following results:

\[ \frac{V_1 \frac{P_1}{T_1}}{V_2 \frac{P_2}{T_2}} = 1 \]

In other words, the "R" disappears. This expression can be transposed, as follows:

\[ \frac{V_2}{V_1} = \frac{\frac{P_2}{P_1}}{\frac{T_2}{T_1}} \]

Example of use of this mathematical expression:

A cylinder contains 10 cubic inches of air at 400 pounds absolute pressure per square inch at a temperature of 600°F. What volume will the air occupy if the temperature is reduced to 60°F (standard temperature) and 14.7 pounds absolute pressure (standard pressure)?

\[ V_2 = ? \]

\[ V_1 = 10 \text{ cubic inches} \]

\[ P_1 = 400 \text{ pounds absolute per square inch} \]

\[ P_2 = 14.7 \text{ " " " " } \]

\[ T_1 = 600 + 459.6°F = 1059.6°F \]

\[ T_2 = 60 + 459.6°F = 519.6°F \]

\[ V_2 = \frac{V_1 \frac{P_1}{T_1}}{P_2 \frac{T_2}{T_1}} = \frac{10 \times 400 \times 519.6}{14.7 \times 1059.6} = 133.4 \text{ cubic inches} \]
Pressure changes may be calculated by:

\[ P_2 = \frac{V_2}{V_1} \times \frac{P_1}{P_2} \times \frac{T_2}{T_1} \]

Avogadro's Principle

Each gas, such as methane, ethane, etc., has a weight, depending on its chemical formula. These weights are called "molecular weights." If carbon has a weight of 12.01 and hydrogen a weight of 1.008, then methane, CH₄, has a molecular weight of:

\[
\begin{align*}
1C & \quad 1 \times 12.01 = 12.01 \\
4H & \quad 4 \times 1.008 = 4.032 \\
\text{CH}_4 & \quad \text{16.042}
\end{align*}
\]

The molecular weight of ethane, C₂H₆, is:

\[
\begin{align*}
2C & \quad 2 \times 12.01 = 24.02 \\
6H & \quad 6 \times 1.008 = 6.048 \\
\text{C}_2\text{H}_6 & \quad 30.068
\end{align*}
\]

In the same way, molecular weights are obtained for all compounds. If the molecular weights are in terms of grams, the molecular weight is called a "gram molecular weight." If pounds are used, the molecular weight is called a "pound molecular weight," or more usually a "pound mol." Pounds mols of several gases follow:

One Pound Mol of

Air = 28.966 pounds
Hydrogen (H₂) = 2.015
Methane = 16.042
Ethylene = 28.052
Ethane = 30.068
Propylene = 42.079
Propane = 44.095
Butylene = 56.105
Isobutylene = 56.105
Butane = 58.121
Isobutane = 58.121

One pound mol of any substance contains the same number of molecules. Avogadro discovered this in connection with gases. His principle states: At the same temperature and pressure a pound mol of any gas occupies the same volume. This follows from the fact that each pound mol of each gas has the same number of molecules in it. Since the molecules have the same spacing at the same temperature and pressure, each gas occupies the same volume.

Pound Mols and Volume

At 60° and standard atmospheric pressure (14.7 pounds absolute per
square inch) a pound mol of any gas occupies 380 cubic feet. This relation is important, since it permits conversion from gas volume to weight. For example, 1000 cubic feet of ethylene measured at 60°F. and 14.7 pounds pressure absolute per square inch is equal to -

\[
\frac{1000}{380} = 2.63 \text{ pound mols}
\]

\[
2.63 \times 28.05 \text{ (molecular weight of ethylene)} = 73.8 \text{ pounds of ethylene.}
\]

**Dalton's Law**

Different gases at the same temperature, provided they do not interact chemically, exert no influence at all upon each other when mixed. Each component of the mixture behaves as if all the others were absent and it alone were in occupation of the whole available volume. If one cubic foot of methane and one cubic foot of steam, both at 15 pounds pressure per square inch absolute, are mixed together, the resulting volume will be two cubic feet and the resulting pressure, of course, remains at 15 pounds; but the methane and steam both act as if they were each at 7.5 pounds pressure per square inch absolute. This may be generalized into Dalton's Law, also called the Law of Partial Pressures, as follows:

The pressure exercised by each component in a mixture of gases is proportional to its concentration in the mixture, and the total pressure of the gas mixture is equal to the sum of those of its components.

A knowledge of this law will be useful in understanding fractional distillation.

**Raoult's Law**

This law will also be useful in understanding fractional distillation. This law has already been presented in part in the section "Effect of Steam on the Vapor Pressure of a Liquid" on page 13. Another illustration of the principal involved follows: Consider the addition of 50 pound mols of a petroleum liquid so heavy it has practically no vapor pressure to 50 pound mols of a volatile liquid with a Reid vapor pressure of 40 pounds per square inch. When the heavy liquid is dissolved in the volatile liquid, each cubic inch of the mixture will contain equal numbers of both kinds of molecules. Thus the concentration of the volatile molecules will be one-half what it was in the unmixed state. This reduces its vapor pressure to one-half, that is, to 20 pounds, one-half the value of the pure volatile compound.

This can be expressed in a general form (Raoult's Law) as follows: The partial vapor pressure of a component over a mixture of miscible liquids is equal to the pound mol fraction of the component in the mixture multiplied by the vapor pressure of the pure component. In a mathematical expression the law becomes:

\[
P_c = pX
\]

where \( P_c \) is the partial vapor pressure of the component under consideration.
P is the vapor pressure of the component in the pure state.

and X is the fraction of the component in the liquid (the fraction in pound mols of the total pound mols).

In this law lies the explanation of how an extremely volatile substance, such as methane, can be present in mixtures such as crude petroleum or cracking coil products at ordinary temperatures and pressures.

Vapor Pressure of Immiscible Liquids

The word "miscible" underlined in Raoul's Law above, means "mutually soluble"; that is, one liquid will dissolve completely in the other just as alcohol will dissolve in water. Water and oil are "immiscible" liquids since water will not dissolve in oil, or oil dissolve in water. Raoul's law does not apply to immiscible liquids. Since water and oil mixtures are encountered occasionally in the refinery, and the results of such encounters are potentially dangerous, it is important that refinery operators understand the effect of heat on immiscible liquids.

The water and oil in a mixture of the two (usually an emulsion) will each exert a vapor pressure of its own, just as though it alone were present. The total pressure existing over the liquid mixture will, therefore, be the sum of these individual pressures. It follows, then, that a pressure equal to the atmosphere will be reached and boiling take place at a temperature below that at which either of the component liquids would boil alone. For example, a still charged with an oil is at a temperature of 180°F. At this temperature the oil creates a vapor pressure of, say, 10 pounds absolute per square inch. Since this pressure is less than atmospheric (14.7 pounds absolute per square inch) the oil does not boil in the still. Water at 180°F. has a vapor pressure of about 7.5 pounds absolute per square inch and consequently it would not boil either. However, if the still contained a water-oil mixture at 180°F (or water is added to the oil in the still) the sum of the vapor pressures of the water and oil would be 10 + 7.5 = 17.5 pounds absolute per square inch. Since this is greater than atmospheric pressure, the contents of the still would boil violently. In all probability, the still would fill with froth and the still contents discharge out the overhead line. Since water is most frequently found in crude petroleum, this effect is encountered during the distillation of crude.

Joule and Thomson's Principle

When gases under high pressure are allowed to expand, they cool themselves slightly. The higher the original pressure, the greater is the cooling effect. This cooling is not to be confused with the cooling that occurs when a liquefied gas (which is usually under high pressure) is allowed to expand. In this case, a large cooling effect is obtained by absorbing heat from the surroundings to change the liquefied gas to vapor (Latent heat).

The cooling of gas by expansion is used to make liquid air. Air is highly compressed and then allowed to expand through the end of a copper coil. The cooled air flows back over the coil, cooling the compressed air in it. This cooled compressed air expands, causing a still lower temperature. This process continues until the air runs from the coil as a liquid.
Liquefaction of Gases: Critical Temperature

As a gas is compressed, the molecules are forced closer together. It should follow that with sufficient pressure, the molecules could be packed close enough together to assume the liquid state. If ethane, for example, at room temperature, is put under a pressure of several hundred pounds per square inch, the gas will change into a liquid. If the ethane gas is at 100°F, it will be found that no pressure, no matter how great, will cause the liquid state to be formed. Thus there is a certain temperature called the "critical temperature" above which pressure will not cause formation of the liquid state. For ethane the critical temperature is 89.9°F. At this temperature a pressure of 717 pounds per square inch will convert ethane gas to liquid ethane. As the temperature drops below 89.9°F, less pressure is required. At the boiling point of ethane (-128.2°F) the liquid will form at standard atmospheric pressure (14.7 pounds per square inch absolute).

Ethylene will be used as the refrigerant in the Butyl Rubber Polymer Unit. When used as a refrigerant it must be liquefied. Evaporation of the liquid ethylene requires heat (latent heat) which it absorbs from the surroundings at the point where evaporation takes place. In order to liquefy ethylene it must be chilled below its critical temperature, 49.5°F. Since water available at Sarnia is not cold enough (rises to about 70°F in Summer) the ethylene must be chilled by evaporation of liquefied ammonia (critical temperature 270.3°F). After chilling below its critical temperature, the ethylene can be converted to a liquid by pressure.

The critical temperatures of various gases and the pressure required at these temperatures to form a liquid are listed below. The pressure required is called the "critical pressure."

<table>
<thead>
<tr>
<th>Gas</th>
<th>Critical Temperature °F</th>
<th>Critical Pressure in atmospheres ♠</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>-116.5</td>
<td>45.8</td>
</tr>
<tr>
<td>Ethylene</td>
<td>49.5</td>
<td>50.9</td>
</tr>
<tr>
<td>Ethane</td>
<td>89.9</td>
<td>48.8</td>
</tr>
<tr>
<td>Propylene</td>
<td>198.1</td>
<td>45.0</td>
</tr>
<tr>
<td>Propane</td>
<td>204.1</td>
<td>43.0</td>
</tr>
<tr>
<td>Isobutane</td>
<td>273.2</td>
<td>37.0</td>
</tr>
<tr>
<td>Butane</td>
<td>307.4</td>
<td>36.0</td>
</tr>
<tr>
<td>Ammonia</td>
<td>270.3</td>
<td>111.5</td>
</tr>
<tr>
<td>Air</td>
<td>-221.6</td>
<td>37.2</td>
</tr>
<tr>
<td>Steam</td>
<td>705.2</td>
<td>217.7</td>
</tr>
</tbody>
</table>

♣ Pressure is frequently recorded in "atmospheres".

1 atmosphere = 14.7 pounds per square inch absolute.

Butanes, pentanes, and heavier hydrocarbons have vapor pressures below 230 pounds per square inch (R.V.P.) and so may be handled as liquids at ordinary temperatures in conventional plant pressure equipment. Methane, ethane, ethylene, propylene and propane, however, develop such high pressures at 100°F that refrigeration is required to keep them at sufficiently low temperatures so that extra heavy pressure equipment is not required.
Liquified gases under pressure, when released to atmospheric pressure, drop in temperature to the normal boiling point. Thus ethylene at 49.5°F and under 750 pounds per square inch pressure, when opened to the atmosphere, drops in temperature to −155 F. At this temperature, ethylene (or any substance) will burn like live steam if it comes in contact with the skin.

Gas Densities

As in the case of solids and liquids, each gas has a characteristic weight per cubic foot. This weight, divided by the weight of a cubic foot of water, gives the specific gravity of the gas. Instead of dividing by the weight of a cubic foot of water, the weight of a cubic foot of air is sometimes used. In this case, the specific gravity of air is 1. Specific gravities of other gases will have values greater or less than 1, depending on if they are heavier or lighter than air. Specific gravities, based on the specific gravity of air = 1, are designated by "Specific Gravity (air = 1).

<table>
<thead>
<tr>
<th>Specific Gravity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
</tr>
<tr>
<td>Methane</td>
</tr>
<tr>
<td>Ethane</td>
</tr>
<tr>
<td>Propane</td>
</tr>
<tr>
<td>Butane</td>
</tr>
<tr>
<td>Air = 1.000</td>
</tr>
<tr>
<td>0.558</td>
</tr>
<tr>
<td>1.049</td>
</tr>
<tr>
<td>1.558</td>
</tr>
<tr>
<td>2.046</td>
</tr>
</tbody>
</table>

Miscellaneous Notes

The vapors of butane and heavier petroleum compounds are relatively very heavy. These vapors will be close to the ground in depressions, trenches, etc., thus forming a fire hazard near furnaces. One gallon of hydrocarbons will form 25 to 45 cubic feet of vapor. These vapors when present in air in a concentration between approximately 1 to 14% by volume, will explode. The explosive range of ethylene is 3 to 29%, hydrogen 4 to 74% and carbon monoxide 12 to 74%.

Each pound of water gives 175 cubic foot of steam. This is 4 to 7 times the volume formed by liquid hydrocarbons. Consequently, relatively small amounts of water in the coils of a furnace will create excessive pressures. Water in stills will occasionally cause the contents to discharge out the overhead line. (See section on immiscible liquids, page 23). This is called a "boil over".

Definitions of Physical Terms

Coagulation:

When solid particles, usually of small size are caused to clump together, the process is called coagulation. Sometimes particles of sludge are formed during the acid treating of wax, that are so small they will not settle out. These particles called "pepper sludge" are coagulated into larger particles that will settle out, by the addition of a small amount of water. The water in this case is sometimes called a "water dropper".
Precipitation:

When very tiny solid particles (collaidol particles) are coagulated into particles large enough to settle out, the settling out is called precipitation. This term is also used to describe the settling out of a solid formed in a solution by chemical reaction. For example, sulphur added to a solution of lead mercaptides in naphtha (formed by the lead-lye treat) causes a precipitate of lead sulphide.

Emulsion

A dispersion of tiny droplets of one liquid in another is an emulsion. An emulsion will form only if the two liquids are not soluble in one another. Water droplets can be dispersed in oil to form a water in oil emulsion. Since the water droplets are separated by the oil, it is sometimes difficult to cause the water droplets to combine into a water layer.

The viscosity of the oil, presence of fine solid particles, various chemicals, etc., all make the emulsion harder to break. By heat and the addition of other chemicals, the emulsion can usually be broken into a water layer and an oil layer. Sometimes emulsions appear to be semi-solid material. Mayonnaise is an emulsion of vegetable oil and water. Emulsions of the consistency of mayonnaise are found in crankcases of motor cars occasionally.

Dew Point

This is the temperature at which a given mixture of air and water vapor is saturated with water vapor. Just below the Dew Point moisture will start to condense out as visible droplets either in the air (fog) or on various objects, such as leaves and grass (dew). In the petroleum industry, dew point refers to the temperature and pressure at which vaporized hydrocarbons in a gaseous mixture will start to condense out.

Superheat

At any given pressure, a certain temperature (Dew Point) must be maintained in order to keep steam as a vapor. Any drop below this temperature and the steam will start to condense to water. Steam at the minimum temperature that will maintain the vapor state is called saturated steam. Steam can be heated much above this minimum temperature. This extra heat is called superheat. The amount of superheat is the temperature of the steam in excess of that corresponding to saturated steam at the given pressure.

Extraction

When a solvent dissolves more of one substance than any other from a mixture of substances, the process is called extraction. For example, phenol will dissolve the undesired components of a raw lubricating oil stock, but will not dissolve the good lubricating components. After mixing the raw stock with phenol, the phenol separates from the desired portion, taking the undesired portion with it in solution. In this way, extraction refines the oil. Extraction processes will be used in several of the plants concerned in the production of synthetic rubber polymers. Sulphuric acid, acetone, and a copper salt solution are examples of the solvents used.
Absorption

When molecules of a gas transfer from the gas to a liquid, the process is called "absorption". If a mixture of gases is in contact with a liquid, those gases with the highest solubility in the liquid will tend to stay in the liquid, while those with low solubility will not build up in the liquid. In this way, certain components can be separated from a mixture of gases. At the Gas Absorption Plant, refinery gases are bubbled through a light oil (menstruum) in which the butanes and heavier have a higher solubility than the propane and lighter hydrocarbons. In this way, the desired butanes and heavier are separated from the propane and lighter. The butanes and heavier are separated as absorption gasoline from the absorption oil by distillation. The absorption oil is used again to process more refinery gases.

Adsorption

If molecules transfer from a liquid or gas to a solid, the process is called "adsorption". Certain solids have a preference for the substances that they will adsorb. Thus charcoal will adsorb certain war gases, but will not adsorb air. In the Clay Contact Plant, clay will preferentially adsorb coloured substances, unsaturated compounds and acids from lubricating oil stocks.

Refrigeration

Refrigeration means creating cold and refers to temperature below the freezing point of water. Commercially this is done by evaporation of volatile liquids called refrigerants, such as liquified ammonia, ethylene, propane, sulphur dioxide, etc. After evaporation, the gases are reconverted to a liquid and used again. The capacity of a refrigerating plant is said to be so many "tons of refrigeration". A plant of one ton capacity could freeze 2000 pounds of water at 32°F into ice at 32°F in 24 hours. The latent heat of fusion of ice is 144 BTU's per pound. A standard ton of refrigeration, therefore, amounts to 288,000 BTU's per 24 hours, or 12,000 BTU's per hour.
DISTILLATION

Distillation is a physical process whereby either pure components or groups of components are separated from a mixture of liquid components. Distillation is used in the refinery to separate groups of components (called the naphtha fraction, kerosene fraction, etc.) from crude petroleum. Some of the distillation units concerned in the production of synthetic rubber polymers will separate a single pure hydrocarbon from petroleum mixtures.

Since about 60% of the total cost of refinery equipment is due to distillation facilities, distillation is the most important operation in a refinery. Consequently, a thorough understanding of distillation should be part of every refinery operator's knowledge. In this section, the principles underlying distillation will be discussed.

Simple and Fractional Distillation

Distillation is used to separate the components of a mixture of liquids, if there is sufficient difference between the boiling points of the components concerned or in more general terms, if there is sufficient difference between the vapor pressures of the components concerned. It is impossible to separate by distillation components whose normal boiling points are the same, or are very close together.

A distillation operation may be carried out by "simple distillation" or "fractional distillation". The essential difference between the methods is that in simple distillation the vapors are removed directly from the still as fast as they are formed, while in fractional distillation the vapors are forced to pass through layers of liquid of approximately the same composition as the vapor, before the vapor leaves the distillation apparatus.

Simple Distillation was the method used in the first refineries. The stills were simply metal tanks (horizontal cylinders or "cheesebox" style) mounted on brick fireboxes. From the top of the still a cast iron "gooseneck" carried the vapor to a condenser. When the crude petroleum in the still started to boil, the first vapors formed consisted for the most part of light naphtha. However, some kerosene and even traces of gas oil were present in the vapor. These were condensed together in the condenser to form the naphtha fraction-the first distillation product. In those days, the refiner's chief problem concerning this fraction was how to get rid of it, since there was little known use for it. As heating of the still continued, the proportion of kerosene and gas oil in the vapor increased, while the proportion of light naphtha decreased. When the proportion of naphtha was considered low enough to produce a relatively non-explosive product when used in a lamp, the condensed vapors were run into a tank labelled "kerosene". This distillate was the chief and frequently the only product taken from crude. Consequently, as much of the crude as possible was distilled into the kerosene tank.

Good separation of components in a mixture of liquids by a single, simple distillation is possible only if the boiling points of the components concerned are very far apart. A distillate obtained from a mixture such as crude petroleum, where the boiling points of the components are very close together, must consequently consist of a large number of different hydrocarbons. The initial boiling point and final boiling point of such a distillate must necessarily be far apart.
Simple distillation is carried out in modern refineries only when a fraction with a wide boiling range is not objectionable or under special circumstances, such as redistillation of a lubricating oil distillate under high vacuum. The rerunning of lubricating oil distillates in Nos. 1 to 6 Vacuum Shell Stills is a simple distillation. By far the greatest amount of distillation today is by the fractional distillation method.

Fractional distillation requires much more complicated equipment than simple distillation. The essential feature of the equipment is a tower up which the vapors from the still can rise. As they rise, they bubble through successive layers of liquid of approximately the same composition as the vapor. This liquid is obtained usually by condensing and cooling some of the vapor leaving the top of the tower and pumping it back into the top of the tower. This liquid is called "reflux." The uprising vapor and downward flowing reflux are thoroughly mixed together as they pass one another, due to the construction of the tower, as will be explained later.

A good separation of the components in a mixture of liquids can be obtained by fractional distillation, even if the boiling points of the components concerned are relatively close together. Fractional distillation of crude thus produces a distillate with a much smaller number of different hydrocarbons than simple distillation. In other words, the initial and final boiling points of a distillate produced by fractional distillation can be quite close together. Such a distillation produces a "close boiling fraction" or a "close cut fraction." When desired, fractional distillation can separate a single pure hydrocarbon, provided its boiling point is not too close to that of another component in the mixture being distilled.

The other advantages of fractional distillation, such as the removal of "side stream" fractions from outlets in the side of the tower and the use of pipe stills instead of shell stills will be discussed later.

Molecular Mechanics of Vaporization and Condensation of a Single Substance

Distillation consists essentially of vaporization and condensation. If these operations (which concern the molecules of a substance) are repeated often enough, as occurs in fractional distillation, a component of high purity can be separated from a mixture of liquids. Consequently, an understanding of the behaviour of molecules during vaporization and condensation is important. Although distillation deals with a mixture of liquids, it is necessary to first explain the behaviour of molecules of a single pure substance, such as water or benzene, during evaporation and condensation. The behaviour of molecules in a mixture of liquids may then be readily understood.

The effect of Heat and Molecular attraction on Evaporation

All liquids are composed of molecules. Each pure liquid is made up of its own kind of molecules. Around each molecule is space in which it can move. Heat causes molecules to move with greater speed. Each molecule has the power to attract or draw to it other molecules. In liquids, the speed of the molecules is low enough so that the attractive forces hold the molecules together. However, the attractive forces are not strong enough to prevent the molecules from moving past one another. The attractive force between molecules depends on the kind of molecules. For example, the attractive force
between benzene molecules is less than that between toluene molecules.

Since molecules in a liquid can move past one another, they can move freely throughout the liquid, but find it difficult to escape from the liquid. At the surface of the liquid, the attractive forces of other molecules tend to pull any molecules attempting to escape back into the liquid. This is illustrated in the diagram below, where the molecules of the liquid are arranged in a symmetrical pattern for illustrative purposes. (Actually the molecules would have a random distribution.)

A molecule (A) in the liquid is completely surrounded by other molecules, each of which exert a pull on the molecule. The attractive forces as shown by the arrows, pull equally in all directions and thus the direction the molecule will move depends on chance only. A molecule at the surface (B) is surrounded only on its lower side by other molecules. These pull this molecule down or sideways. Thus, when this molecule moves, the chances are it will go back into the liquid.

The attractive force of a molecule on another has a limited range. If a molecule can get beyond the range of the attractive forces of other liquid molecules, it can then lead an independent existence, such as (C) in the diagram. Liquid molecules do escape from the attractive forces of surrounding liquid molecules. This occurs when a liquid molecule near the surface has sufficient speed to break through all the attractive forces of neighbouring molecules, and reach the vapor space above. The liquid molecule thus becomes a vapor molecule.

Not all molecules in a liquid travel with the same speed. Collisions and the action of the attractive forces between molecules cause some molecules to move faster, others to be slowed or even momentarily stopped. Thus the molecules in a liquid are moving at many different speeds, which change from instant to instant. (When these various speeds are, theoretically, added together and then divided by the number of molecules, the average speed of the
molecules results. The average speed of the molecules is proportional to the temperature. As the average speed changes, so does the temperature. If a molecule is travelling faster than a certain minimum speed and is near the surface of the liquid, it will have sufficient energy to overcome the attractive forces of neighbouring liquid molecules and escape into the space above. At low temperatures, not many of the molecules get above the minimum speed necessary to escape. As heat is added to the liquid, more molecules reach the necessary speed and thus escape.

The escape of molecules from the surface of a liquid is evaporation.

Cooling Due to Evaporation

During evaporation the temperature of the liquid drops. This follows from the fact that the high speed (hot) molecules are the ones to escape leaving behind the slower and colder molecules. In the tropics cool water is obtained by keeping water in a jar which is sufficiently porous to let the water wet the outside of the jar. Evaporation of this water on the outside of the jar removes the high speed molecules, thus continuously cooling the water. The cooling due to evaporation can be experienced by wetting one's hand with a volatile liquid such as a light naphtha and allowing the naphtha to evaporate.

Equilibrium in a Closed Container

Despite the fact that molecules continually escape from a liquid, no more than a definite number ever collect in the space above the liquid in a closed container at a given temperature. Since molecules are continually escaping, it might reasonably be expected that more and more would collect in the vapor space. That they do not collect is due to the fact that vapor molecules return to the liquid. When as many molecules per second return to the liquid as escape from the liquid, the number of molecules in the vapor space must be constant. This number is all the molecules the space will hold at the particular temperature, that is, the space is saturated with vapor molecules. If the temperature of the liquid is raised more molecules escape and a new number is required to saturate the space. When the number of escaping molecules is equal to the number of returning molecules, the liquid is said to be in "equilibrium" with the vapor. The number of molecules escaping is dependent on the temperature. Thus a different state of equilibrium is reached for each temperature. Since the number of molecules in the vapor space at each equilibrium is a constant, the vapor pressure (dependent on the number and speed of the molecules) must also be a constant for a given temperature. For example, the pressure in a Reid Vapor Pressure Bomb is read only after equilibrium is established between the liquid and its vapor when the temperature is 100°F.

When a mixture of miscible liquids is in equilibrium with its vapor, the vapor has a particular composition depending on how much of each kind of material is in the liquid mixture. (See Raoult's Law). A state of non-equilibrium exists when too much or too little of one component exists in the vapor space. For example, some of the benzene molecules that should be in the vapor above a liquid benzene-toluene mixture may be some distance down in the liquid. Since it takes time for these molecules to work their way to the surface and to saturate the vapor space, it follows that time is frequently necessary for equilibrium to be established. This time can be reduced if all parts of the liquid can be quickly exposed to the vapor. This can be done by shaking the liquid into the vapor space. Intimate contact between vapor and liquid is thus desirable since it establishes equilibrium quickly - or in other words, produces vapor of the proper composition in a minimum time.
Vapor Pressure and Boiling

As explained above, molecules which escape from a liquid form the vapor which exists over any liquid. If the liquid and vapor are enclosed, these high speed vapor molecules strike the walls of the container, causing a vapor pressure that can be measured by a pressure gauge in terms of pounds per square inch or inches (or centimetres) of mercury. Even when there is no containing vessel, the vapor molecules strike the air molecules, causing the same vapor pressure. In general, vapor pressure is the tendency of a liquid to pass into the vapor state, or in other words, the tendency of a liquid to evaporate. The it increases as the liquid is heated and decreases as the liquid is cooled. Raising the temperature of a liquid increases the speed of the molecules, so that more molecules leave the liquid. Thus there is a larger proportion of the molecules in the vapor space and a consequent increase in the vapor pressure. As the temperature of the liquid is raised, the molecules move faster and faster, and more and more molecules escape into the vapor space. Finally the liquid begins to boil; that is, bubbles of vapor form in the body of the liquid and rise to the surface. When boiling occurs the temperature will not rise any higher until all the liquid has been vaporized, if the liquid is a single pure substance. The heat added is all used up in converting the liquid into vapor (latent heat). If the liquid is heated more strongly, it boils harder, but does not get any hotter.

As the temperature is raised to the boiling point, vaporization occurs only from the surface of the liquid, because vapor cannot exist in the body of the liquid when its vapor pressure is less than the pressure imposed on it. The imposed pressure is usually that of the air. At the boiling point, however, the vapor pressure becomes equal to the atmospheric pressure, and so bubbles of vapor form below the surface and rise to the top. The boiling point of a liquid is thus defined as the temperature at which the vapor pressure of the liquid equals the pressure exerted on the liquid by its surroundings. If the liquid is boiled in an open vessel, the pressure exerted by the surroundings is the atmospheric air pressure, 14.7 pounds per square inch at sea level. If the liquid is boiled in a closed container, thus causing a high pressure in it, the boiling point must, by our previous definition, be much higher than if the vessel were open. If a vacuum pump is connected to the boiler, and part of the air above the liquid is pumped out, the pressure exerted on the liquid will be lower, and the vapor pressure of the liquid will become equal to the surrounding pressure at a lower temperature. Thus the boiling point of a liquid can be changed by altering the pressure on it. This is done in several refinery distillations.

The graph below shows the vapor pressure curves of water, benzene and toluene. From such curves, the vapor pressure of pure substances at any temperature can be found. Such curves also show the absolute pressure required to cause a substance to boil at any desired temperature. For example:

<table>
<thead>
<tr>
<th>Temperature in °F. to cause boiling at</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 p.s.i.</td>
</tr>
<tr>
<td>Water</td>
</tr>
<tr>
<td>Benzene</td>
</tr>
<tr>
<td>Toluene</td>
</tr>
</tbody>
</table>

p.s.i. = pounds per square inch.
When no pressure is mentioned, it is understood that the pressure is atmospheric. The boiling point at atmospheric pressure is known as the "normal boiling point."

Condensation

A liquid in a closed container can be completely boiled into vapor, provided the container is large enough or strong enough to hold the vapor. The molecules of this vapor are widely separated. All are travelling with high speeds, due to the average temperature necessary for their existence. When they collide they bounce from one another with the same high speed. In the liquid state these molecules were held close together by the attraction each molecule had for its neighbours. This was so because the average temperature of the liquid was not high enough to give all the molecules sufficient speed to break away from one another. In the vapor state the molecules are travelling so fast that they are able to overcome the attraction each time they collide. If the vapor molecules that collide are both travelling with the same speed, they bounce from one another without loss in speed. If a fast (hot) molecule hits a slow (cold) molecule, the fast molecule is slowed down (cooled) and the slow one speeded up (heated). In a condenser, the slow molecules are those making up the walls of the condenser tubes. As the temperature of the vapor is lowered, the vapor molecules lose their speed until the slowest ones are no longer able to resist the attractive forces exerted when they come close together. Consequently they join together to form liquid again. As heat is taken from the vapor (by the vapor molecules striking the cold walls of the condenser tube and rebounding with greatly reduced speeds) more molecules are slowed down to the point where they adhere to one another when they collide. In this way the vapor is reconverted to the liquid.
This process, the reverse of evaporation, is condensation.

If the pressure on the vapor is atmospheric pressure, the temperature to which the vapors must be cooled for condensation to take place is the same as the normal boiling temperature. If the pressure on the vapor is greater than atmospheric, condensation takes place at temperatures above the normal boiling point; the greater the pressure imposed, the higher the temperature at which condensation occurs. (Condensation will not take place above a certain temperature, which has a particular value for each substance and is known as the "critical temperature" of the substance). The lower the pressure (vacuum) on the vapor, the lower the temperature to which the vapor must be cooled before condensation takes place.

**PRINCIPLES OF DISTILLATION**

The discussion so far has dealt with the behaviour of a single pure substance, such as water. Distillation, however, is concerned with mixtures of liquids. The liquids in a mixture may be miscible (soluble in one another) or immiscible (insoluble in one another). Particular laws of distillation apply in each case. Petroleum is a mixture of miscible liquids, consequently the distillation of miscible liquids is of first importance to the petroleum industry.

The principles of separation of miscible liquids by distillation will be explained by discussing a mixture of benzene and toluene. The principles which apply to this two-component mixture of miscible liquids will also apply to the distillation of petroleum, which consists of many miscible components.

In a benzene-toluene mixture, there are two kinds of molecules, each of which has its characteristic power of attracting other molecules. Some of both kinds of molecules will be escaping from (evaporation) and returning to (condensation) the liquid until equilibrium is established. Thus, the liquid mixture will have a definite vapor pressure, depending on the temperature. Examination of the vapor pressure chart shows that benzene has a normal boiling point of 176°F, while toluene has a normal boiling point of 230°F. It might seem, then, that if the mixture were heated to 176°F, all the benzene would boil out and could be condensed in a separate container, thus separating the benzene from the toluene. This, unfortunately, does not happen. As pointed out before, there are some molecules which move faster than others, and these high speed molecules break out of the liquid into the vapor space. Since both benzene and toluene molecules can reach the necessary speed at any temperature, both kinds can escape from the liquid mixture. Raising the temperature will increase the numbers of both kinds of molecules in the vapor.

An analysis of the vapor formed at any temperature would show more benzene molecules are present than toluene molecules. Since both kinds of molecules do not get sufficient speed to escape from the liquid mixture, why is the vapor richer in benzene molecules? The answer is the fundamental reason why distillation can separate the components in a mixture of miscible liquids and applies to simple and fractional distillation methods.

The answer lies in the smaller power of the benzene molecules to attract other molecules to it. The forces of attraction between a benzene molecule and those surrounding it are less than the forces of attraction between a toluene molecule and its neighbours. Therefore, a benzene molecule needs less energy (i.e. lower speed) to break away from its neighbours than does a toluene molecule. At any given temperature, more benzene than toluene...
molecules will reach the necessary speed requirement to escape from the liquid state. Consequently, the vapor will contain more benzene than toluene molecules and the total vapor pressure due to the mixture of liquids will be caused more by benzene molecules than by toluene molecules.

That part of the vapor pressure caused by benzene (partial pressure of benzene) is less than it would be if benzene only were present. The greater attractive force of the toluene molecules not only prevents toluene molecules from entering the vapor space as readily as benzene molecules, but holds back some of the benzene molecules as well. Thus the toluene causes a decrease in the vapor pressure of benzene. Benzene, of course, has a similar but lesser effect on the vapor pressure of toluene. The vapor pressure of any mixture of benzene and toluene, therefore lies somewhere between the vapor pressures of the pure liquids. The partial vapor pressure due to either the benzene or toluene, or of the total vapor pressure of the liquids together, can be determined by Raoult's Law. Raoult's Law states that the vapor pressure of any component of a mixture of liquids is the vapor pressure of the pure liquid at the same temperature multiplied by its mol fraction in the liquid, or

\[ P_c = P \times X \]

where
- \( P_c \) = vapor pressure of one component in the mixture
- \( P \) = vapor pressure of the component as a pure substance at the same temperature.
- \( X \) = mol fraction of the component in the liquid.

This law merely means that for the benzene-toluene mixture, the vapor pressure of the benzene depends on the amount of benzene present; i.e., if the mixture is 90 mol % benzene, the vapor pressure due to the benzene is nearly that of pure benzene, while if the mixture is only 10 mol % benzene, the vapor pressure due to the benzene is very small.

Simple Distillation

The vapors formed by boiling a mixture of miscible liquids are removed directly from the still in simple distillation. The vapors have a higher proportion of the molecules of the lower boiling component than existed in the liquid or, in other words, the vapor is richer in the lower boiling component. Consequently, a certain amount of separation of the two components has taken place. If the enriched vapors are condensed and a part of the condensate again distilled, further separation occurs due to the second vapor being still richer in the lower boiling component. Repeated redistillations will finally produce a small amount of the lower boiling component as a single pure substance.

The amount of enrichment may be demonstrated by determining the composition of the vapor formed by distillation of a benzene-toluene mixture. This is done by reading the composition of the vapor formed at the boiling temperature by a given mixture of benzene and toluene from an Equilibrium Liquid-Vapor Composition chart, as shown below. The vertical scales at the ends of the horizontal lines in this chart represent temperatures. Horizontally across the bottom is a scale which shows the amount of benzene in all possible mixtures of benzene and toluene in mol percent. Across the top the amount of toluene is shown. The horizontal scales apply to both liquid and vapor compositions.
Mol percent is obtained from the mol fraction. The mol fraction is found by dividing the number of mols of the component concerned by the total number of mols in the mixture. (One mol is the molecular weight of the component; it may be expressed in pounds). If a mixture of benzene and toluene contained 1 mol of benzene and 4 mols of toluene, the mol fraction of benzene would be:

\[ \frac{1}{1 + 4} = \frac{1}{5} = 0.2 \]

Similarly the mol fraction of toluene in this example would be 0.8. The sum of the mol fraction must always equal 1. The mol percent is obtained by multiplying the mol fraction by 100. Thus a mol fraction of 0.2 is equivalent to 20 mol percent.
The curves on the chart show the relationship between composition of the liquid and vapor mixtures and the temperature. The lower curve (liquid) shows the temperature at which all mixtures of benzene and toluene will boil at atmospheric pressure. For pressures other than atmospheric, other curves are required. The upper curve (vapor) shows the composition of the vapor produced when a given mixture of benzene and toluene boils. The horizontal temperature lines connect the composition of the vapor with the composition of the particular liquid mixture that is boiling. For example, a mixture of 20 mol % benzene and 80 mol % toluene boils at 216°F, as shown on the chart. The vapor formed from this mixture has the composition indicated by the junction of the 216°F temperature line and the vapor curve. This junction shows the vapor must contain 38 mol % benzene and consequently 62 mol % toluene.

At the right edge of the chart the composition is 100% benzene, i.e. pure benzene, with no toluene in it. If the temperature is raised to 176°F, the benzene will boil and the composition of the vapor will be 100% benzene.

At the left edge the composition is 100% toluene, which boils at 230°F. Consider a mixture of 20 mol % benzene and 80 mol % toluene contained in a still. On applying heat to this mixture, it will start to boil at 216°F, and the temperature of the vapor will also be 216°F. As explained above, the horizontal 216°F line shows the composition of this vapor to be 38 mol % benzene and 62 mol % toluene. This is a very important fact, because it shows that, although the vapor coming from any mixture of liquids contains both components, it is richer than the original mixture in the component with the higher vapor pressure (and lower boiling point). That is, the vapor contains 38 mol % benzene, as compared to only 20 mol % in the liquid. Only a relatively small amount of vapor of this composition can be taken from the still. Vapors that follow will be less rich in benzene. If all the contents of the still were vaporized, the vapor would, of course, have the same composition as the original liquid. Consequently, the smaller the amount of vapor removed, the richer it will be in benzene.

The vapor may be condensed to a liquid by cooling in a separate container. If this liquid, containing 38 mol % benzene, is heated again (redistilled) it will start to boil at 204°F. and the first vapor coming off will have a composition of 60 mol % benzene. By two partial vaporizations and two complete condensations a liquid containing 60 mol % benzene has been separated from an original liquid with 20 mol % benzene. By repeating the process a number of times, (redistillation) the final product will be pure benzene, but the quantity obtained will be only a small fraction of the original mixture.

Returning to the original material, and remembering that the first vapor coming off contained more benzene than the original liquid mixture, it is obvious that the material left in the still must be richer in toluene than the original, because more benzene than toluene has vaporized. This increase in the relative amount of toluene in the residue in the still is toluene enrichment of the bottoms.

Enrichment due to Partial Condensation

Separation of the components in a mixture of vapors can take place due to condensation. If a mixture of benzene-toluene vapors is cooled until it has all condensed, the composition of the condensed liquid will of course, be the same as the composition of the vapor. But if the mixture is cooled only enough to condense part of the vapor, the condensed (liquid) portion will be found richer in toluene than the original vapor. Since toluene molecules have a greater attractive force than benzene, the tendency will be for the toluene molecules to adhere together in greater numbers than the benzene mole-
cules at any temperature to which the vapor mixture is cooled. The uncondensed vapor must, therefore, be richer in benzene, and it can be drawn off to another condenser. Both partial vaporization and partial condensation will give enrichment. If these two processes are repeated often enough, the final products are pure materials. These are the fundamental processes by which separation of miscible liquids take place.

Simple Distillation and Heat Exchange

In this and following sections the development of simple distillation into fraction distillation will be shown. The first step is to show how heat exchange can take place in simple distillation.

Figure A. of the diagram below shows a simple distillation unit, consisting of three stills and a condenser. This arrangement of stills demonstrates the way in which the heat added to the first still can be passed on to other stills and thus cause several distillation operations to proceed. Still 1 contains 20 mol % benzene and 80 mol % toluene; still 2 contains 40 mol % benzene and 60 mol % toluene; and still 3 contains 65 mol % benzene and 35 mol % toluene. Heat is supplied to still 1 until the liquid mixture boils ($216^\circ F$). The vapors leave this still at $216^\circ F$, and enter the coil immersed in the cold liquid in still 2, where the vapors are condensed. Condensation releases the latent heat of the vapors, consequently the liquid in still 2 is heated. This exchange of heat between the vapors from still 1 and the liquid in still 2 soon causes the latter to reach a temperature of $203^\circ F$, which, as the chart on page 9 indicates, is the boiling point of the 40 mol % benzene - 60 mol % toluene mixture there. Thus a second still is set in operation by heat added to still 1.

![Development of a Bubble Tower]
Still 2 forms vapors with a composition of 63 mol % benzene and 37 mol % toluene, as may be found from the chart. These vapors on condensing in the coil in still 3 give their heat to the liquid there. This exchange of heat causes a temperature of 191°F., at which temperature the 65 mol % benzene - 35 mol % toluene mixture there boils. This produces a vapor with 82 mol % benzene. This is condensed in the condenser to produce, in this case, the final distillate. Repetition of the process in more stills would finally produce 100% pure benzene. All the distillations would have been accomplished by the heat originally added to the first still. This demonstrates the principle of heat exchange in distillation. The idea is carried further in the next section.

Note that separation by simple distillation in the three stills above took place by three partial evaporations. Partial condensation had no part in the separation obtained.

**Fractional Distillation**

It will have been noticed that the composition of the vapor condensed in the coil in any still had approximately the same composition as the liquid in the still. Consequently, the vapors from still 1 could be bubbled directly into the liquid in still 2. The vapors would condense giving up their heat to the liquid, and by condensing simple increase the amount of liquid of approximately 40 mol % - 60 mol % composition in the still. Similarly the vapors from still 2 could be added directly to the liquid in still 3. By permitting the coils to discharge into the stills, the liquid levels in stills 2 and 3 must rise as still 1 boils dry. To prevent this, return pipes connect stills 2 and 1 and stills 3 and 2. This system is shown in figure B.

The still battery in figure B forms a unit in which continuous distillation takes place. Heat is supplied to still 1 only. A benzene-toluene mixture is fed continuously into still 3 at the point labelled "Fresh Oil". As this feed flows from still 3, to still 2 to still 1, it is heated by heat exchange and thus subjected to partial evaporation. The feed in turn acts as a cooling medium on the vapors rising from stills 1 and 2 thus causing partial condensation of these vapors. Enrichment is thus caused by both partial vaporization and partial condensation. The vapors from still 1 bubble into the liquid in still 2, where part of it is condensed. The heat thus liberated vaporizes part of the liquid there. The vapors so formed and the vapors from still 1 that did not condense in still 2 bubble into still 3, where the process is repeated. A vapor rich in benzene leaves still 3 to be condensed in the condenser to produce a distillate product. From the bottom of still 1, a toluene rich product is drawn off as a residue or bottoms product.

In this system of distillation, two partial condensations have been used in addition to three partial vaporizations. Consequently, as may be expected, a greater degree of enrichment is obtained in this system than in simple distillation, where partial evaporation only takes place. When separation is aided by partial condensation caused by bubbling the vapors from one still through cooler liquids in the next still, the distillation process is known as "fractional distillation." When partial vaporization and partial condensation take place in this manner, heat exchange also occurs. This is the third factor that characterizes fractional distillation. Fractional distillation, however, involves another factor, as will be explained next.

The vapor from still 3 in figure B, is contaminated by a variable amount of toluene from the feed which enters the system at this point. Since this contamination of the benzene-rich overhead vapor is undesirable, three
more stills are added, giving the arrangement in figure C. In this arrangement, the final overhead vapor is taken from still 6. This still contains a partial condenser, which condenses some of the vapors leaving the still, in particular any toluene vapor. This condensed vapor falls back into the still as liquid and flows from the bottom of the still into still 5 and so on down. In this way, liquid is kept in stills 4, 5 and 6. The vapors from still 3 then bubble through these liquid layers and is subjected to three extra partial condensations. Since heat exchange takes place partial vaporization goes on also. Consequently, a much greater degree of separation of the components is obtained.

If there were no liquid in stills 4, 5 and 6, these stills would then serve no purpose at all. Consequently liquid of a composition approximately the same as the final overhead vapors must be put into the final still. This liquid, which is returned to the top still, and which is necessary for fractional distillation to occur in stills 4, 5 and 6 is called "reflux."

Distillation Towers

The arrangement of six stills is unsatisfactory from a practical standpoint. It involves a large amount of piping, and separate supports for all the stills. The same result can be accomplished more satisfactorily by placing the stills on top of one another, thus making a single tower or column. Instead of separate stills, the tower is fitted with horizontal perforated plates, usually called "trays." These trays, as in the case of the separate stills, are connected by pipes permitting liquid to flow to the tray below. Fitted into each perforation in a tray is a short "riser" or "vapor neck" surmounted by a "bubble cap," which causes the vapors from below to bubble through the liquid on the tray. One type of bubble cap assembly is shown below.

The tray that is equivalent to still 3 in figure C on page 11 is called the "feed tray," since this is the point at which the fresh feed enters the system. That portion of the tower above the feed tray (equivalent to
stills 4, 5 and 6) is called the fractionating or rectifying section; that below is called the stripping section. Some towers, such as the crude tower of the Sarnia Topping and Coking Unit, have no stripping section, since the feed enters at the bottom of the tower. Others, such as a depropanizer have no fractionating section since the feed enters at the top of the tower. Nevertheless, the principles of fractionation apply to both the stripping and rectifying sections. The term stripping indicates that the desired product, which is subjected to fractional distillation, is removed as a bottom product. The term rectification indicates that the desired product which is subjected to fractional distillation, is removed as an overhead product. A distillation tower with rectifying and stripping sections is illustrated in the diagram on page 15.

The arrangement of trays and bubble caps in a tower is known by various names, such as "Distillation Tower," "Rectifying Tower," "Distillation Column," "Bubble Tower," "Fractional Distillation Tower" and "Fractionator." Distillation towers may be as high as 150 feet and contain up to 70 trays. The number of bubble caps per tray may be from a few to 5,000 depending on the size of the tray. A distillation tower for crude petroleum such as the crude tower of the Sarnia Combination Topping and Coking Unit will contain 26 trays with 100 bubble caps on each tray.

In the bottom of a typical distillation tower such as illustrated, there is a layer of oil which is caused to boil by heat from steam coils or by heat carried into the tower by the feed. The vapors from this oil rise through the risers on the first tray and are caused to mix with the liquid there by the bubble caps. This liquid which is slightly cooler than the vapors, condenses only the heaviest fractions in the vapors. The uncondensed vapors bubble through the oil to the tray above, where this "scrubbing" action is repeated and slightly lighter components are condensed. In this way, vapors go up the tower, the oil on each tray scrubbing the vapors which pass through and progressively condensing heavier fractions. The vapors that condense collect on each tray, until they overflow into the "downspouts" and drop to the tray below, which is slightly hotter. It is evident that the constant heating which results from the upward passage of hot vapors will tend to reboil any lighter components that have dropped back as liquid from the plate above. They thus become vapor again and rise to bubble through the tray above, where the heaviest portions are again condensed. This recondensing and revaporizing goes on continuously, on each tray in the tower. Only the lightest fractions finally escape the top tray and come off as an overhead vapor. Only the heavy ends remain liquid in their passage to the bottom tray, where they are drawn off. Thus a product rich in low boiling (high vapor pressure) components is separated as a vapor from a liquid product rich in high boiling (low vapor pressure) components in a fractional distillation tower.

Reflux

Refineries use three methods of obtaining reflux. These are illustrated on page 16. The first is the one described previously, where part of the vapors rising from the top tray are condensed in a partial condenser and fall back as "hot reflux." Sometimes all the vapors are taken overhead, condensed and cooled, and part of this cold liquid pumped back to the top tray, the rest being removed as distillate product. This is the "cold reflux" method. "Circulating reflux" is the term applied when liquid is removed from one tray, cooled, and pumped back to the same, or an adjacent tray. The cold liquid flowing into the hot tower condenses some of the vapor passing that tray, and so increases the amount of liquid flowing down from the tray. Circulating
reflux is often used to reflux trays part way down a tower. When so used, it may be called "Intermediate Reflux." It is also used to reflux the top of a tower where it is desired to keep the diameter of the tower of reasonable size. If all the material required for reflux and overhead product existed in the upper part of the tower as vapor, a large diameter tower would be required to hold the vapor. By drawing off hot liquid, cooling it and returning it as liquid, the reflux does not enter the vapor state, thus a smaller tower can be used.

Reflux is essential for the operation of a distillation tower. The example of the six stills showed that if no reflux is returned to the top of a column, there is no liquid on the trays above the feed tray, and consequently no enrichment of the vapors rising through those trays. Instead of acting as a fractionating column, such a tower is only an expensive piece of large pipe.

Vapors will not contact or mix with the liquid on the trays unless forced to do so. Thus, if the liquid level on the trays is lower than the tops of the slots in the bubble caps, the vapors will escape through the openings left without mixing with the liquid. In this case, no heat exchange, no partial evaporation, no partial condensation, and consequently no fractional distillation occurs. A dam or weir about the downspout keeps the liquid level on each tray at a proper level. When the level is correct the vapors on bubbling through the liquid cause it to froth up.

Types of Reflux used on Distillation Towers
Section 4

If a tray is tilted or otherwise disarranged, so that the proper liquid level is not maintained all over the tray, practically all the vapors will pass through the areas where the least liquid is encountered. Thus, little or no fractional distillation takes place. A gas that follows a path of least resistance (i.e., no encounters with liquids on the trays) is said to channel. The vapors follow one channel up and the liquids another channel down—with little or no mixing of the two streams. Trays with holes in them or chimneys without caps will permit channelling to take place.

Tower temperature control is maintained by controlling the temperature of the overhead vapor and the temperature of the heated feed to the tower. The overhead vapor temperature is varied by changing the amount of reflux pumped into the tower. An increase in the amount of reflux causes a drop in temperature.

Reflux also has an important effect on the degree of separation or enrichment effected in the tower. If more reflux is put back into the tower, the scrubbing action on the rising vapors is increased, and a purer fraction (i.e., more closely cut fraction) is obtained. However, increasing the reflux reduces the amount of product obtained from the tower and increases the fuel consumption. Consequently, the most economical operation is to operate a tower with the minimum reflux that gives the necessary degree of separation of the components.

Side Streams

When a distillation tower is operating under constant conditions of feed composition and temperature, a liquid of constant composition is formed on each tray. If the liquid on any tray has a composition which makes it suitable for use as a petroleum product, the tray may be tapped and the liquid drawn off. A product obtained in this way is called a side stream product. Several side stream products may be taken from a tower. Three side streams are removed from the crude tower of the Sarnia Topping and Coking Unit. As a rule, four or more trays separate trays from which side stream products are taken. A product is withdrawn from the 8th tray from the top of the tower, where the liquid has the composition required for water white. This, after further treatment, is kerosene. By withdrawing from the 10th tray instead of the 8th, a product suitable for stove oil is obtained. A light gas oil and a heavy gas oil are withdrawn from about the 18th and 24th trays respectively.

If too much is withdrawn as a side stream product, the liquid level on the trays concerned may fall to a point where the bubble cap slots are not covered. In this case, mixing of the vapors and liquid will not occur and fractionation will not take place, as explained before.

Side stream products always contain a small amount of low boiling components dissolved in them. This is so because the light fractions (low boiling) are continuously bubbling through the liquids on their way to the top of the tower. Consequently, some of the light material remains in solution in the liquid drawn off as a side stream product. In some products, these low boiling components are objectionable and must be removed. They are removed by passing the side stream product into the top of a "stripper", a short distillation tower with approximately 4 trays. As the product cascades from tray to tray, it is scrubbed by uprising steam. As will be described later on, the steam removes the low boiling components. References to naphtha which would give water white a dangerously low flash point are removed in this manner.
Section 4

EQUILIBRIUM IN DISTILLATION UNITS

(a) Batch Stills

As explained before, a vapor and its liquid are in equilibrium when as many molecules escape from the liquid as return to the liquid. When this occurs the vapor from a mixture of liquids (such as benzene and toluene or petroleum) has a particular composition depending on the concentration of each component in the liquid mixture (Raoult’s Law). A liquid mixture in a closed container will, sooner or later, be in equilibrium with the vapor it produces. If, however, some of the vapor molecules are allowed to escape from the container, there will be fewer molecules in the vapor space and hence a smaller number to return to the liquid. In this case more molecules escape from the liquid than return to it and equilibrium is no longer maintained.

Consequently, distillation is carried out in a batch still under a non-equilibrium condition since vapor is continuously removed overhead. This is one reason why a close boiling fraction cannot be obtained from a batch still by a single distillation. If the overhead is shut off, equilibrium would of course be established, but this would be upset as soon as the overhead is again opened. The less vapor allowed overhead, the closer the approach to equilibrium and the better the distillation as far as purity of the overhead product is concerned.

(b) Distillation Towers

A much closer approach to equilibrium can be made and maintained in distillation towers despite the fact that vapors are continuously removed from the tower. In this case, the feed stock which enters the tower continuously makes up the loss of vapor going overhead. Consequently, there is a relatively constant number of molecules in the vapor space and thus molecules can enter and leave the liquid in approximately equal numbers. This effect takes place on each tray in the tower.

Perfect equilibrium is, of course, not obtained, although it is usual to speak of a tower being under "equilibrium" conditions. Many factors will cause the equilibrium to be more or less upset in the tower. The more intimate the mixture of the vapors and liquids on the trays, the better the equilibrium. The design of the bubble caps determines in a large measure the amount of mixing. The longer the time of contact between vapor and liquid the better the equilibrium. This is accomplished by reducing the velocity with which the vapors rise up the tower (making the still run slower.)

A tower may be operating under a certain set of equilibrium conditions such as amount of reflux, coil outlet temperature, etc. Some of the conditions may be changed. For example, the coil outlet temperature may be reduced, or a side stream product withdrawn. When this occurs, the existing equilibrium is upset but a new equilibrium is established which is characteristic of the new set of conditions. Thus certain operating conditions may be changed with only the formation of a new equilibrium. Other conditions may change, such as an increase in the amount of vapor in the tower over a certain maximum, dry trays, plugged bubble caps, etc., which prevent any equilibrium from being established.

EFFECT OF PRESSURE AND VACUUM ON DISTILLATION

Fundamentally, vacuum and pressure have no effect on distillation except to change the temperature at which boiling takes place. The exchange of heat, partial evaporation and partial condensation which characterize fractional distillation, take place regardless of the pressure or vacuum on Page 10
the tower.

A distillation tower distilling low boiling products may be operated under sufficient pressure so that the overhead vapors will condense in the condenser at a reasonable temperature. The Sarnia Debutanizer is operated under 150 pounds per square inch in order to condense the propane and heavier in the overhead at a temperature obtainable by water. Operation of the tower at atmospheric pressure would require a large amount of refrigeration to condense the overhead vapors.

Vacuum is maintained in the Vacuum Flash Coil Units to cause boiling at relatively low temperatures. The lubricating oil components in the charge stock (reduced crude) would require temperatures over 1000°F. in order to boil at atmospheric pressure. At such temperatures the lubricating oil components would be decomposed by cracking. By vacuum, the components are caused to boil at 800°F. where cracking is negligible.

In addition to lowering the temperature of distillation and prevention of possible decomposition, vacuum distillation causes more complete separation of components in a mixture. Fractionation is more effective under vacuum (therefore at low temperatures) because there is a larger difference between the vapor pressures of the components at low pressures than at high pressures. This is illustrated in the following tabulation for propane and pentane. The relative tendency for propane to leave the liquid when at −50°F. is about four times as great as when the mixture is distilled at 450°F. (Note: From Table, $5.3 \div 1.3 = 4$ approximately).

This in part may account for the fewer trays used in vacuum towers.

<table>
<thead>
<tr>
<th>Component</th>
<th>Vapor Pressures in Cm. of Mercury</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>at −50°F.</td>
</tr>
<tr>
<td>Propane</td>
<td>63.0</td>
</tr>
<tr>
<td>Pentane</td>
<td>1.2</td>
</tr>
<tr>
<td>Ratio V.P. Propane : V.P. Pentane</td>
<td>5.3 : 1.3</td>
</tr>
</tbody>
</table>

**EFFECT OF STEAM ON DISTILLATION**

It was shown previously that molecules have a tendency to escape from liquids to form vapor, this tendency being called vapor pressure. In a closed vessel the vapor space above a liquid will become saturated with a definite number of molecules when equilibrium between the liquid and vapor is established at a definite temperature.

From the above it is evident that if means are provided to remove the vapor that collects in the vapor space, the equilibrium would be upset and more molecules would leave the liquid (evaporate) to set up a new equilibrium. By continuously sweeping out the molecules that escape from the liquid, distillation can take place even though the vapor pressure of the liquid by itself is not enough to lift the vapors out of the distillation unit. Since continuous evaporation takes place, the liquid is continuously cooled. To maintain a constant temperature in the liquid during evaporation, heat must be supplied to the liquid.
Section 4

This is the process that takes place during steam distillation, i.e. the addition of open steam to a batch still or a distillation tower. The steam is the means whereby the vapor molecules are removed from the still. An oil at a temperature where its vapor pressure is less than atmospheric pressure (or the pressure imposed on the still) will have its vapor molecules carried out of the still and thus distillation takes place.

To compensate for the cooling during evaporation, heat must be supplied to the still by fire or other means (fire and steam distillation). Steam is admitted to the still below the surface of the liquid to agitate the liquid and to cause equilibrium to be established more quickly. The steam and the oil vapor molecules leave the top of the still or distillation tower to be condensed in a condenser. The more steam injected into the still, the more oil vapor will be carried and thus the still "runs faster". In this case, evaporation is more rapid and more heat must be added to compensate for the increased cooling due to evaporation. The addition of more heat will cause the still to run faster due to increased evaporation. Even if the temperature of the still falls, the action of the steam causes distillation to go on, but at a slower rate. If, however, the injection of steam is stopped, distillation stops entirely.

Since distillation is occurring at a temperature below the normal boiling point of the oil, it is evident that the steam causes the same effect as the application of vacuum. By combining steam distillation with vacuum oils with a very low vapor pressure even at high temperatures (such as Paraffin Distillate 180/190) can be distilled.

Steam is the usual substance added to stills to sweep out the vapor molecules. However, any gas that doesn't chemically react with the oil could be used. Hydrocarbon vapors from an outside source could be injected. Furthermore the vapors created by the oil in the still itself act in the same way as steam. Crude for example has a relatively large amount of light material which vaporizes relatively easily. This, just as would steam, carries with it molecules of heavier oil components which are at temperatures well below their normal boiling point.

Even air at ordinary temperatures acts in a similar manner on tanks of volatile liquids. Air getting into and out of a tank carries with it the vapor molecules in the space above the liquid. Consequently, volatile liquids should be stored in air tight tanks.

FLASH DISTILLATION

In flash distillation the charge stock is heated in a confined space to a temperature such that part of it changes to vapor. When the mixture of liquids and vapours leaves the confined space, the vapors separate or flash from the liquid portion. By heating to a suitable temperature only the required portion of the charge stock changes to vapor. This vapor may be subjected to fractional distillation in a distillation tower.

The mechanism of flash distillation is most readily described in terms of evaporation. Consider crude petroleum passing through the coil of a pipe still. This coil is an example of the confined space referred to above and will be described in more detail in a later section. Heat is applied till the vaporization point is reached, i.e. vapor is formed which occupies space in the coil. As determined by the vapor pressure of each component,
this space will contain vapor molecules of all components in the crude; even though the boiling point of some of the components has not been reached. As more heat is applied, the vapor space expands, the vapor pressure of the liquid components increases and a larger proportion of the heavier components evaporates into the vapor space. The lighter material by evaporating first forms a vapor space into which the heavier components can evaporate. The light material by forming a vapor space and then carrying along the heavier molecules thus acts in a manner similar to steam in steam distillation.

This latter point is important in the operation of a flash distillation unit. The amount of vapor in the pipe still coil near its discharge end is considerable. Consequently, it tends to occupy more space than the unvaporized oil. In order for the increased volume to leave the coil in the same quantities as the cold oil enters the coil, the mixture of hot liquid and vapor must travel at a higher velocity. The resulting increase in friction between the turbulent mixture and the coil walls causes a drop in pressure. This pressure drop may be sufficiently great near the discharge end of a coil to cause excessive evaporation due to the reduced pressure. When evaporation takes place cooling occurs. This cooling may be great enough to cause a drop in temperature near the coil outlet. It is a common observation that the location of the region of maximum temperature may be some distance back in the coil rather than at the coil outlet. It will be appreciated that even though the temperature drops somewhat as the coil outlet is approached, heat will be absorbed by the oil from the furnace. This heat is used as latent heat to convert the liquid into vapor, i.e. cause evaporation.

When extremely high boiling oils must be vaporized, means are taken to reduce as much as possible the pressure in the coil and in the transfer line between the coil and the tower. This reduction in pressure causes more evaporation of the high boiling oils forming vapors which can be subjected to fractional distillation. The reduction in pressure may be obtained for example, by dividing the coil into two parallel sections near the discharge end. This extends the low pressure area farther back into the furnace. In some cases where the flash tower is under vacuum, the vacuum may extend into the coil, thus aiding evaporation. Live steam may be added to the coil to assist evaporation as already described. By the use of an extra large transfer line pressure build-up due to friction in this region is partly removed.

A decrease in pressure in the transfer line promotes further evaporation. Since no heat is supplied to the transfer line, the cooling due to evaporation causes an appreciable temperature drop. Consequently, the temperature in the flash zone in a flash tower is lower than the coil outlet temperature.

In both steam distillation and flash distillation means are available for obtaining vapors of substances with high boiling points which by themselves would not boil under the particular conditions of temperature or pressure available or permissible.

Flash distillation will be used in practically all of the distillation units concerned in the production of synthetic rubber polymers. Since the materials to be distilled are, for the most part, liquified gases, the high temperatures created by pipe still furnaces are not required. Charge stocks to distillation towers may consequently be heated in a tube and shell arrangement by means of steam. Instead of steam, heat exchange with a hot liquid may be used or latent heat of condensation obtained by condensing a vapor in the shell. When heat is obtained by the latter method the heating equipment is called a "vaporizer".
**DISTILLATION OF IMMISCIBLE LIQUIDS**

So far the behaviour of miscible liquids only has been considered. It was shown that in such mixtures, the vapor pressure of a given component depended on the mol fraction of that component in the liquid, and might be small indeed if the fraction were small. In other words, the mixtures considered so far have followed Raoult's Law.

However, in cases where the liquids are immiscible (i.e. oil and water) Raoult's Law does not apply; each component of the mixture behaves independently of the other as if each were present alone. Thus at a given temperature the total vapor pressure is the sum of the individual vapor pressures, no matter how much or how little there is of each component present. This is of importance in an oil refinery as it explains why pressures become so high even if only a trace of water is present, whereas the same mol percentage of a light hydrocarbon has little, if any, effect. Another point regarding water is that due to its low molecular weight, a relatively small amount gives a large amount of vapor. For example, 18 (one pound mol) of water produces the same amount of vapor as about 100 pounds (one pound mol) of naphtha.

**REFINERY DISTILLATION EQUIPMENT**

**Batch Stills**

The simplest refinery distillation unit is a single batch still, as described under Simple Distillation on page 1. The still, known as a shell still, is directly heated by a fire under the still. The vapors formed pass directly from the still to a condenser, which cools the fractions that come off one after another. Such a distillation unit has several disadvantages, such as:

(a) Production of one product at a time.
(b) Poor utilization of heat.
(c) Poor quality of fractions.
(d) Necessity of redistilling fractions.
(e) Requires continuous close supervision.
(f) Still must be cooled and cleaned after each batch is distilled.

The quality of the fractions obtained from a batch still can be greatly improved (closer cut) by passing the vapors from the still into a bubble tower. Reflux is formed, as described previously, and fractional distillation takes place. The heavy ends that collect in the bottom of the bubble tower flow back into the still.

In general, batch stills are used for special rerunning operations, or where only a small volume (500 to 2,000 barrels) of material must be distilled. Examples of batch stills equipped with bubble towers at the Sarnia refinery are the stills making up the #9 - 12 Rerun Battery.

**Continuous Shell Still Battery**

By connecting several shell stills into a battery, several of the disadvantages of a single batch still are overcome. For example, the distillation process is continuous (may last six months) and several products are produced at the same time. By placing bubble towers on each of the stills, the quality of the products obtained may be improved to the desired level. Since...
the process is continuous, better utilization of heat is obtained by heating the charge stock by using it as the cooling medium to condense and cool the vapor products from each still.

The shell stills are connected, so that the feed stock flows continuously through one still after another. Each still is at a higher temperature than the previous one, consequently a higher boiling product is removed by each still as the feed stock moves through the battery. The Continuous Crude Shell Still Battery (Nos. 17 - 23 Stills) at No. 1 Plant, which can process 20,000 barrels per day, is a typical example. Crude, after being preheated by exchange of heat with the products from the stills in the battery, and after passing through a flash tower, enters No. 17 still. The temperature is such that for the time the crude remains in the still all the naphtha is converted to vapor. This leaves the still by way of an attached bubble tower. The bottoms in No. 17 still are then passed into No. 18 still, which is at a higher temperature. Here the water white fraction is vaporized. The residue from this still enters the next still, which is still hotter, and a still higher boiling fraction is vaporized. In this way, the crude is advanced through the battery, while undergoing continuous distillation. The residue from the last still amounts to some 40% of the crude and is distilled for its lubricating oil and asphalt content.

Since the level of the oil in each still of a shell still battery remains constant, flue tubes running the length of each still carry the hot gases from the firebox, through the oil, to the stack. In this way more heat is obtained from the fire.

Pipe Stills

The modern method of heating a charge stock to a distillation tower, where high temperatures are required (such as in crude distillation) is by means of a pipe still. A pipe still is also known as a "tube still", "tubular heater", "heating coil" and "flash coil". Regardless of the name, the heating of the charge stock takes place in a series of pipes or tubes fastened to the walls and ceiling of a furnace. The tubes which receive heat by direct radiation from the flames of the gas or oil burners of the furnace are in the "radiant section" of the furnace. Those protected from direct radiation by a brick firewall receive heat by contact with the hot gases produced by combustion of the fuel. These tubes are in the "convection section" of the furnace.

The charge stock passes at high velocity (turbulent flow) through the tubes. During this passage, which may take up to five minutes in the many hundreds of yards of tubing in the furnace, the oil is quickly heated to the desired "coil outlet" temperature. The small volume in the tubes permits rapid and exact control of the temperature of the stock, as it enters the distillation tower. Unlike a shell still, local overheating of the stock does not occur in the pipe still. A modern pipe still designed to handle twice as much crude petroleum in a day as a continuous shell still battery will require only two-thirds as much fuel and one-fifth as much steam. By the short time under the action of heat less decomposition of the charge takes place than in a continuous battery.

The pipe still permits heating the charge stock to such a temperature that all the desired products flash into vapor (flash distillation) when the heated stock enters the distillation tower. By subjecting these vapors to fractional distillation in large towers designed for the purpose, all the desired products may be obtained as an overhead product, a bottom product and several side stream products. This occurs in the separation of the primary fractions from crude in the Kellogg crude tower.
Gasoline Fractionators

Very light hydrocarbons are fractionated in equipment somewhat different from that just described. These towers take a feed which contains relatively few hydrocarbons (methane to heptane or octane usually) and cut it into very definite and narrow ranges. Because the products are so sharply defined, sidestreams are not drawn off, as their removal would disturb the equilibrium of the products being fractionated. Since the feed is quite low-boiling, it is heated sufficiently by passing through heat exchangers before admission to the tower. The liquid from the bottom of the tower is drawn off to a "reboiler" in which it is boiled by steam coils, and the vapors formed are passed into the bottom of the tower again. Usually no open steam is used in gasoline fractionators.

Examples of this type of distillation equipment are the Debutanizer and Stabilizer at the D.S. & A. Plant, the Column Steam Stills, and various fractionating columns in connection with the rubber project.

Gasoline fractionators usually operate under pressure because the light materials coming overhead have normal boiling points lower than the temperature of the water used in the condensers, so they cannot be condensed except at pressures above atmospheric.

Vacuum Towers

Lube distillates are decomposed if heated to their normal boiling points. Consequently, to distill them at all, refineries resort to vacuum distillation, with steam. The equipment is the same as that used to distill crude in pipe stills, except for modifications necessitated by the low pressure used.

Distillation Terms

Capacity of Distillation Tower

The capacity of a fractionating tower may be limited by the maximum quantity of liquid that can be passed downward, or by the maximum quantity of vapor that can be passed upward, per minute, without upsetting the normal functioning of the tower. The liquid flow downward may be limited either by the capacity of the weirs and downspouts, or by the resistance to the flow by vapor through the bubble trays. The vapor capacity may be limited either by the resistance to flow through the plates, or by the quantity of entrainment that can be tolerated.

Pressure Drop Through Tray

Resistance to the flow of vapor through a bubble tray is made up of the head of liquid above the top of the slots in the caps and the frictional resistance in the vapor path. The latter is determined by the eddy currents caused by the design of the cap. The resistance to the flow of the vapor causes a loss in pressure of the vapors, as they pass through a tray. If the loss in pressure becomes great enough, the vapors will be unable to pass through the trays and the tower becomes inoperative.
Priming or Flooding

Normally the head of liquid in the downspout is great enough to overcome any tendency of the vapors to rise up the downspout. If for any reason the resistance to the flow of the vapor through the tray is increased to a high enough value, or the amount of vapor forced into the tower is too great, the vapors will then pass up the downspouts. When this occurs, the tower is said to "prime" or "flood". "Fuking" is a colloquial term meaning the same thing, but indicates liquid is carried out the overhead vapor line.

Entrainment

Entrainment is the upward carrying of liquid droplets by the vapor. It usually shows up as an impairment of color or the overhead or sidestream product. The liquid particles may be formed by vapor jets from the bubble cap slots, or by bursting liquid bubbles. The tiny droplets so formed are mechanically carried by the vapor to the next tray where they impair fractionating efficiency by causing a higher proportion of heavy ends to be present on the tray.

Plate Efficiency

Plate (or tray) efficiency is the ratio of the separation obtained by an actual plate to the separation effected by some standard plate. The separation or enrichment effected by the standard plate is that obtained when the liquid and vapor are in perfect equilibrium and the mechanical conditions are ideal. The Standard Plate is sometimes referred to as a Theoretical Plate.

Equilibrium

When the rate with which molecules escape from a liquid (evaporation) is exactly equal to the rate with which they return to the liquid (condensation) the liquid-vapor system is said to be in equilibrium. For perfect equilibrium, every molecule of liquid in the tower must come in contact with every vapor molecule to give a perfect distribution of molecules in the vapor and liquid states. Since long contact time and intricate mechanical means are required to approach this condition, equilibrium is not attained in an actual distillation tower. Equilibrium is closely approached in special laboratory distillation apparatus, where the column can be operated for long periods of time under total reflux.

Total Reflux

In a batch operation, the overhead product can be condensed and all of it returned to the top of the tower. When no overhead product is taken off, the tower is said to operate under total reflux.
PROCESSING EQUIPMENT

I - DISTILLATION EQUIPMENT

1. Bubble Towers

The heart of any refinery distillation unit is the bubble tower, which has been described and illustrated in Section 4 - "Distillation". Bubble towers vary greatly in size and constructional details. Gasoline fractionators, which handle non-corrosive materials at relatively low temperatures, are usually built of mild steel plate, the shell being rolled and butt-welded, with the trays welded in, and the risers rolled into the trays. Crude towers handle more corrosive material at high temperatures, so their trays are made of cast iron, with the risers cast integral with the plate. Almost all the caps used in refinery bubble towers are made of cast iron, because cast iron has greater corrosion resistance than pressed steel. Caps need not be circular, but may be square or rectangular in shape. Rectangular caps 18 or more inches long over rimmed slots in the tray are a relatively new development known as tunnel type bubble caps. Caps of this type are used on the Kellogg unit and the bubble tower of the new #9 cracking unit.

When a refinery operator speaks of the "size" of a tower, he is referring to its diameter, not to its height, because the tower capacity is controlled by its diameter.

2. Shell Stills

The oldest and simplest form of still is the shell still, which consists of a horizontal tank, about 15" diameter by 42' long, mounted on a brick firebox, which may be fired at either or both ends, using oil or gas as fuel.

On the still itself is a safety valve and a vapor line leading to the bottom of the overhead equipment (usually a small bubble tower). A return line takes liquid from the tower to the still.

Shell stills may be operated either in batch or continuous processes. The batch method is the oldest. A batch still has a charging line into the still proper, and is operated as a single unit.

By connecting several shell stills in series, a continuous battery is obtained. The bottoms from each still are pumped by a steam lift (described later) into the bubble tower of the next still. The chief difference between a batch still and a continuous battery lies in the heating method. Each still in a continuous battery maintains a constant oil level, while the batch still starts with the still full, and boils off material until only a heavy residue comprising as little as 10 - 20% of the charge is left. Because the continuous shell still keeps a constant volume, it is possible to utilize more of the heat supplied by inserting pipes or flues in the bottom half of the still. The products of combustion pass along the bottom of the still, up the back and through the flues in the still, then to the stack. The drawoff and charging lines to each still in a continuous battery are cross-connected, so that any still may be by-passed without interfering with the operation of the others. Steam is injected into the bottom of each still to agitate the oil and prevent overheating, and to assist in the distillation of the oil. A typical shell still is illustrated on Page 2.
Sarnia Refinery uses the following shell stills:

Numbers 1 - 6  - Vacuum Stills. (Nos. 1 - 4 have flues and may be used as a continuous battery)

Numbers 9 - 12  - Atmospheric Rerun Stills.

Numbers 17-23  - Continuous Crude Battery.

Numbers 35-38  - Herun Stills. These have flues and are operated in a continuous manner.

3. Pipe Stills

The most modern development in heaters is the pipe still, which is a furnace with banks of tubes running across the walls and roof, and with other tubes in the flue gas outlet. The oil is heated as it flows rapidly through the tubes. As the diagrams show, all pipe stills have two sections, a radiant section in the furnace body proper, where one or at most two rows of tubes absorb heat directly from the flames, and a convection section, where a number of rows of tubes absorb heat from the hot gases going to the stack. In addition, there may be several rows of tubes through which steam is passed, in order to obtain superheated steam for stripping. The following indicates two types of pipe still furnaces.
Some of the heating duties for which pipe still furnaces are used, are:

1. Heating crude for atmospheric flash distillation with coil outlets up to 750°F.

2. Heating reduced crude for vacuum flash distillation with outlet temperatures up to 800°F.

3. Heating cracking coil tar for vacuum flash distillation for the production of asphalt, with outlet temperatures up to 780°F.

4. Heating cracking coil stock up to 1100°F
Section 5

One of the major uses for pipe stills is in the processing of crude at atmospheric pressure. In this service the hot, partly vaporized crude is discharged from the pipe still into a crude bubble tower, such as in the Kellogg Combination and Topping Unit (see flow diagram in Section 8). The distinguishing characteristics of crude towers are:

1. They are required to process large amounts of wide-boiling range crude into comparatively broad cuts, so the towers are large in diameter, but contain relatively few plates (the Kellogg crude tower has 26 plates).

2. The feed is admitted as a mixture of liquid and vapor from pipe stills.

3. Steam is admitted to the bottom of the tower to strip light ends from the bottoms.

4. Side streams are withdrawn at two, three or more points in the column and taken, if necessary, to separate strippers.

5. Frequently, though not always, an intermediate reflux is supplied to the centre part of the tower.

All side streams except the heaviest ones, usually pass through strippers to have the light materials (naphthas) removed, otherwise the kerosene and light gas oil drawn off would have low flash points. A side stream stripper is a small tower fitted with from three to six bubble cap trays. The material to be stripped is poured in on the top tray, steam is blown in at the bottom, rises through the tower removing light ends from the hydrocarbon stream, and passes out the top to a condenser. The water is separated from the oil in the condenser and the oil run back into the crude tower. The stripped oil comes out the bottom of the tower, and is pumped to storage.

If two or three side stream strippers are required for one crude tower, their construction is simplified by building all of them in one tower. Each stripper is separate from the others, but all of them have a common shell. In this case, the steam-oil vapor lines coming overhead from each stripper are joined and pass to a common condenser.

4. Rerun Stills

A rerun still is any distillation apparatus used to refractonate cuts from a previous still - usually cuts from a crude tower. By this definition a rerun still may be either batch or continuous, either vacuum or atmospheric. Thus, there are rerun batch shell stills, rerun vacuum shell stills, rerun atmospheric towers and rerun vacuum towers.

At Sarnia Refinery there are a variety of rerun stills. The Kellogg unit has a Rerun Tower with a reboiler to refractonate overhead from the crude tower. The Column Steam Still (see flow diagram in section 8) is a continuous rerun tower for naphthas. The batch shell stills are listed below.

Numbers 35 to 38 Rerun Stills are shell stills fitted with bubble towers. Nos. 35, 36 and 37 are used for rerunning aviation base stocks, and No. 38 is used for rerunning cumene. Although the bubble towers on these stills are equipped with partial condensers, it is customary to use pumpback (cold) reflux when rerunning aviation stock.

Numbers 9 to 12 Rerun Stills are used for reducing Canadian crude cylinder stock, rerunning longtime burning oil and mineral seal oil, as well as reducing
Other lube oil stocks. Stills 9 and 10 were formerly equipped with bubble towers, but the trays have been removed from them, and thus they act solely as expansion drums.

Numbers 1 to 6 Vacuum Stills are used for rerunning lubricating oil distillates, and can be used as batch units, or operated as a continuous battery. These shell stills are smaller and are strongly braced on the inside to prevent collapse when operating under vacuum. The overhead equipment consists of expansion chambers known as entrainment drums or mist separators, and tubular condensers, which could be used as partial condensers. Vacuum is maintained on these stills by barometric leg condensers, and steam jet ejectors.

5. Flash Stills

High-boiling materials such as lube stocks and asphalts must be distilled under vacuum to avoid cracking. The continuous apparatus for this service is the vacuum flash still. The material is heated in a pipe still furnace from which it discharges into a bubble tower maintained under vacuum by jet ejectors and barometric leg condensers, operating at the top of the tower. As the hot material enters the vacuum tower, the vapors separate or "flash" from the liquid portion of the hot material. It is from this behaviour that the equipment gets its name.

Vacuum flash towers are constructed like crude towers, except that their diameter has to be greater for similar throughputs. Care must be taken in the design to keep the pressure drop through the trays and vapor lines as small as possible, otherwise the pressure at the bottom of the tower will be considerably greater than the pressure at the top. The material at the bottom of the tower may decompose due to the increased temperature caused by the increased pressure. Sarnia Refinery has two vacuum flash stills for processing reduced crude to lube stocks. (See Section 8)

6. Debutanizer

The debutanizer is the first unit in the Debutanization, Stabilization Plant, which processes pressure distillate to remove the more volatile light ends and dissolved gases. The debutanizer is so called because its purpose is to remove gases (methane to propane) and the C4 cut overhead, leaving pentanes and heavier in the bottoms. The Sarnia debutanizer is operated to take pentanes and lighter overhead, leaving hexanes and heavier in the bottoms.

The debutanizer is a carefully designed bubble tower, built to operate under pressure, because the volatile hydrocarbons which pass overhead cannot be condensed with ordinary cooling water, except at pressures of from 100 to 250 pounds per square inch. The feed of pressure distillate and coke still distillate is preheated in exchangers, and put in about half way up the tower. The reboiler is a small pipe still, through which liquid from the tower bottom is circulated. The bottoms from the debutanizer is a stable, low vapor pressure cracked naphtha.

7. Stabilizer

The stabilizer is the second unit in the D.S.& A. Plant. It is similar to the debutanizer in construction, except that its reboiler is steam heated. The feed to the stabilizer is the overhead from the debutanizer, which contains methane to pentane inclusive. A part of the gases in the debutanizer