Crude Oil Distillation

1. Overview of crude oil distillation

The crude oil stills are the first major processing units in the refinery. They are used to separate the crude oils by distillation into fractions according to boiling point so that each of the processing units following will have feedstocks that meet their particular specifications.

- Higher efficiencies and lower costs are achieved if the separation of the crude oil is accomplished in two steps as shown in Fig .1:
  1. Fractionating the total crude oil at essentially atmospheric pressure.
  2. The high-boiling bottoms fraction (topped or atmospheric reduced crude) from the atmospheric still to a second fractionator operated at a high vacuum.

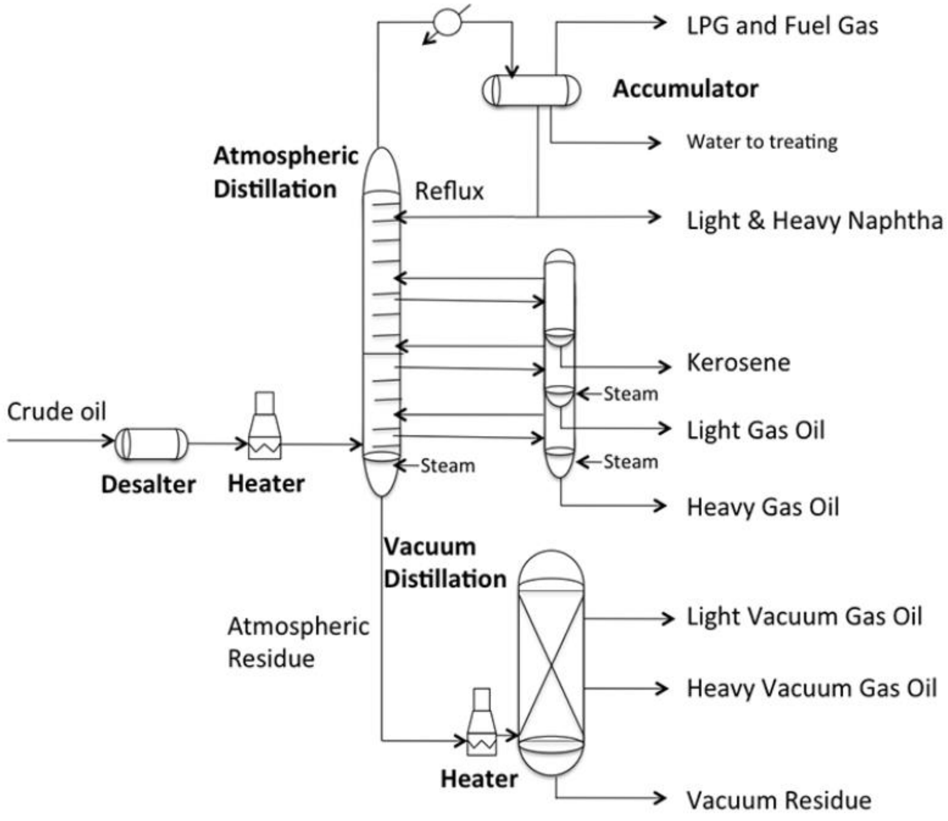


Figure 1. Atmospheric and Vacuum Distillations

Vacuum distillation still is employed to separate the heavier portion of the crude oil into fractions, because the high temperatures necessary to vaporize the topped crude at atmospheric pressure cause thermal cracking to occur, with the resulting loss to dry gas, discolouration of the product, and equipment fouling due to coke formation.

Typical fraction cut points and boiling ranges for atmospheric and vacuum still fractions are given in Table 4.1 and Table 4.2.

TABLE 4.1
Boiling Ranges of Typical Crude Oil Fractions at Atmospheric Pressure

Fraction	Boiling ranges, °F (°C)	
	ASTM	TBP
Butanes and lighter		
Light straight-run (LSR) naphtha	90–220 (32–104)	90–190 (32–88)
Heavy straight-run (HSR) naphtha	180–400 (82–204)	190–380 (88–193)
Kerosine	330–540 (166–282)	380–520 (193–271)
Light gas oil (LGO)	420–640 (216–338)	520–610 (271–321)
Atmospheric gas oil (AGO)	550–830 (288–443)	610–800 (321–427)
Vacuum gas oil (VGO)	750–1050 (399–566)	800–1050 (427–566)
Vacuum reduced crude (VRC)	1050+ (566+)	1050+ (566+)

TABLE 4.2
TBP Cut Points for Various Crude Oil Fractions

Cut	IBP °F (°C)	EP °F (°C)	Processing use
LSR gasoline cut	90 (32)	180 (82)	Min. light gasoline
	90 (32)	190 (88)	Normal LSR cut
	80 (27)	220 (104)	Max. LSR cut
HSR gasoline (naphtha)	180 (82)	380 (193)	Max. reforming cut
	190 (88)	330 (166)	Max. jet fuel opr.
	220 (104)	330 (166)	Min. reforming cut
Kerosine	330 (166)	520 (271)	Max. kerosine cut
	330 (166)	480 (249)	Max. jet-50 cut
	380 (193)	520 (271)	Max. gasoline operation
Light gas oil	420 (216)	610[a] (321)	Max. diesel fuel
	480 (249)	610[a] (321)	Max. jet fuel
	520 (271)	610[a] (321)	Max. kerosine
Heavy gas oil (HGO)	610 (321)	800 (427)	Catalytic cracker or hydrocracker feed
Vacuum gas oil	800 (427)	1050 (566)	Deasphalter or catalytic cracker feed
	800 (427)	950 (566)	Catalytic cracker or hydrocracker feed

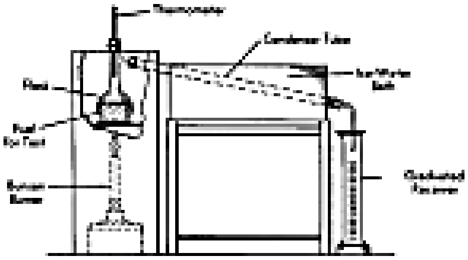
2. Basic Input Data

2.1 ASTM Distillation

- ASTM distillation is carried out in a relatively simple apparatus consisting of a flask holding the sample connected to an inclined condenser, which condensed the rising vapours.

- The fractions distilled are collected in a graduated cylinder.
- The temperature of the rising vapours is recorded at a specific interval of the collected distillates.
- This is essentially a batch distillation with one equilibrium stage and no reflux and the minimum separation of the components of the fractions.
- The temperature at which the first drop of condensate is collected is called the initial boiling point (IBP).
- The endpoint (EP) is the maximum vapour temperature when almost the entire sample is distilled (above 95%).
- For gasoline, kerosene, gas oil and similar light and middle distillates, the *ASTM method D86*, which is carried out at atmospheric pressure, is used.
- Heavy petroleum products, which tend to decompose in the *ASTM D86 method* but can be partially or completely vaporized at a maximum temperature of 400 °C (750 °F) and pressures down to 1 mm Hg, are distilled using the *ASTM D1160 method*. It is carried out at pressures between 1 and 760 mm Hg.
- Minimum fractionation occurs in ASTM distillation, and components in the mixture do not distil one by one in the order of their boiling points, but rather as mixtures of successively higher boiling points.

- يتم تقطير ASTM في جهاز بسيط نسبيًا يتكون من دورق يحمل العينة المتصلة بمكثف مائل ، مما يؤدي إلى تكثيف الأبخرة المتصاعدة.
- يتم جمع الأجزاء المقطرة في أسطوانة متدرجة.
- يتم تسجيل درجة حرارة الأبخرة المتصاعدة على فترات زمنية محددة من نواتج التقطير المجمعة.
- هذا نوع من التقطير في الأساس عبارة عن تقطير دفعي (الوجبات) بمرحلة توازن واحدة وبدون ارتداد وفصل أدنى لمكونات الكسور الجزئية .
- تسمى درجة الحرارة التي يتم عندها تجميع القطرة الأولى من المكثفات نقطة الغليان الأولية (IBP).
- يطلق مصطلح النقطة النهائية (EP) والتي تمثل أقصى درجة حرارة للبخار عندما يتم تقطير العينة بأكملها تقريبًا (أعلى من 95٪).
- بالنسبة للبنزين والكيروسين وزيت الغاز ونواتج التقطير الخفيفة والمتوسطة المماثلة ، يتم استخدام طريقة ASTM D86 ، والتي يتم إجراؤها تحت الضغط الجوي.
- يتم تقطير المنتجات البترولية الثقيلة ، التي تميل إلى التحلل في طريقة ASTM D86 ولكن يمكن تبخيرها جزئيًا أو كليًا عند درجة حرارة قصوى تبلغ 400 درجة مئوية (750 درجة فهرنهايت) وضغوط تصل إلى 1 ملم زئبق ، باستخدام طريقة ASTM D1160. يتم إجراؤه عند ضغوط تتراوح بين 1 و 760 ملم زئبق.
- يحدث الحد الأدنى من التجزئة في تقطير ASTM ، حيث يتم تقطير المكونات الموجودة في الخليط واحدًا تلو الآخر بترتيب نقاط غليانها ، بل على شكل خليط من نقاط الغليان الأعلى على التوالي.



2.2 True Boiling Point Distillation(TBP)

- The data from TBP distillation provides a more detailed characterization of the volatility of crude oil or petroleum fraction.
- TBP is performed in columns with 15 theoretical plates or equilibrium stages and a reflux ratio of 5.
- Rising vapours are condensed and collected either at a constant rate of boiling points or a constant rate of the sample vaporized.

- The operation of the TBP at 760 mm Hg for boiling points below 400 °C (750 °F).
- For higher boiling point fractions, the distillation is conducted at reduced pressures as low as 0.5 mm Hg.
- Results from vacuum operations are extrapolated to atmospheric pressure.
- The high degree of fractionation in this test gives an accurate component distribution.
- Because the degree of separation for a TBP distillation test is much higher than that of the ASTM distillation test, its IBP is lower and its EP is higher than those of the ASTM test.
- The TBP curve (a plot of the NBP versus the per cent volume of sample distilled) is usually used as a basis for the characterization of crude oil or a petroleum product for design and analysis.

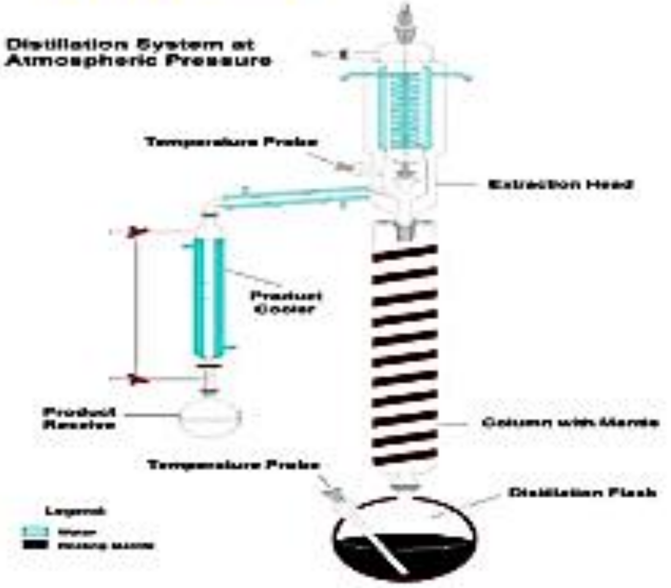


Figure 3 True boiling point (TBP) distillation system

- توفر البيانات المأخوذة من تقطير TBP توصيفًا أكثر تفصيلاً للتطبيقات الفعلية الخام أو تجزئة البترول.
- يتم تنفيذ TBP في أعمدة تحتوي على 15 لوحة نظرية أو مراحل توازن ونسبة ارتداد 5.
- تكثف الأبخرة المتصاعدة وتجمع إما بمعدل ثابت لنقاط الغليان أو بمعدل ثابت للعينة التي تتبخر.
- تشغيل TBP عند 760 ملم زئبق لنقاط الغليان أقل من 400 درجة مئوية (750 درجة فهرنهايت).
- بالنسبة للكسور ذات درجة الغليان الأعلى ، يتم التقطير عند ضغوط منخفضة تصل إلى 0.5 ملم زئبق.
- يتم استقراء نتائج عمليات التفريغ للضغط الجوي.
- درجة التجزئة العالية في هذا الاختبار تعطي توزيعًا دقيقًا للمكونات.
- نظرًا لأن درجة الفصل لاختبار التقطير TBP أعلى بكثير من اختبار التقطير ASTM ، فإن IBP لتقطير TBP يكون أقل و EP أعلى من اختبار ASTM
- عادة ما يستخدم منحنى TBP (وهو مخطط بين NBP الى النسبة المئوية لحجم العينة المقطرة) كأساس لتوصيف النفط الخام أو المنتج البترولي لغرض التصميم والتحليل.

2.3 Conversion between ASTM and TBP Distillation

Since TBP distillation is both tedious and time-consuming in comparison with the ASTM method, there has been an incentive to develop a correlation to convert ASTM to TBP distillation while at the same time achieving the benefit of the detailed separation of TBP with the little effort of the ASTM distillation.

بما إن التقطير بطريقة TBP معقد ويستغرق وقتًا طويلاً مقارنة بطريقة ASTM ، فقد كان هناك حافز لتطوير الارتباط لتحويل ASTM إلى تقطير TBP مع تحقيق فائدة الفصل التفصيلي لـ TBP مع تقليل في الجهد وفي نفس الوقت تقطير ASTM.

The following equation suggested by *Riazi and Daubert (1980)* and published by the *API (1993)* is used for the interconversion, referred to as the *API method*:

توضح العلاقة بين تقطير TBP و تقطير ASTM والتي اعتمدت من قبل API والمعروفة بعلاقة *Daubert* كما في المعادلة (4.1):

$$TBP = a(ASTM\ D86)^{b} \quad \ldots\ldots\ldots\ldots(4.1)$$

where a and b are constants varying with per cent of liquid sample distilled as given in Table 4.3.

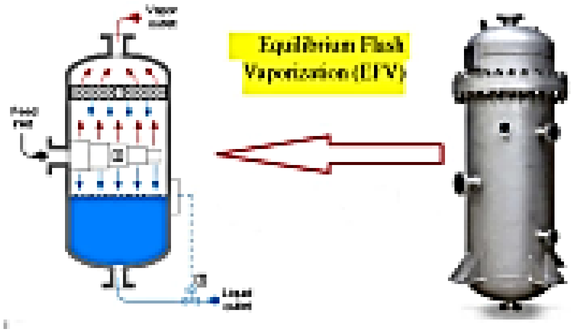
Table 4.3 constant of equation (4.1)

Volume % distilled	*a*	*b*
0	0.9167	1.0019
10	0.5277	1.0900
30	0.7429	1.0425
50	0.8920	1.0176
70	0.8705	1.0226
90	0.9490	1.0110
95	0.8008	1.0355

- TBP is true boiling point temperatures at 0, 10, 30, 50, 70, 90, and 95 volume per cent (v %) distilled, in degrees Rankin.
- ASTM D86 is the observed ASTM D86 temperatures at corresponding volume per cent distilled, in degrees Rankin.
- The average error between the calculated and measured TBP is in the range of 5 °C (41 °F).

2.4 Equilibrium Flash Vaporization (EFV)

- Is a single-stage separation technique.
- A liquid mixture feed is pumped through a heater to raise the temperature and enthalpy of the mixture.
- It then flows through a valve and the pressure is reduced, causing the liquid to **partially vaporize**. Because the vapour and liquid are in such close contact up until the "flash" occurs, the product liquid and vapour phases approach **equilibrium**.



- هي تقنية فصل تتألف من مرحلة واحدة.
- يتم ضخ خليط سوائل من خلال مسخن لرفع درجة الحرارة والمحتوى الحراري للخليط.
- يتدفق بعدها خليط السوائل عبر صمام ويقل الضغط ، مما يؤدي إلى تبخر السائل جزئيًا. نظرًا لأن البخار والسائل على اتصال وثيق حتى يحدث "الوميض" ، تقترب مراحل السائل والبخار المنتج من التوازن.

2.5 Conversion between EFV to ASTM Distillation Curves

- To convert the boiling temperature from ASTM to EFV, equation (4.2) is applied.

$$\boxed{EFV = a\,(ASTM)^{b}\,(sp.gr)^{c}} \quad \ldots\ldots\ldots\ldots(4.2)$$

- The temperature should be in Rankin (°R)
- Table (4.4) is used to find the constants (a,b, and c) in equation (4.2)

Table (4.4) constant for equation (4.2)

Vol%	*a*	*b*	*c*	ASTM D 86 range,°C
0	2.9747	0.8466	0.4209	10–265
10	1.4459	0.9511	0.1287	60–320
30	0.8506	1.0315	0.0817	90–340
50	3.2680	0.8274	0.6214	110–355
70	8.2873	0.6871	0.9340	130–400
90	10.6266	0.6529	1.1025	160–520
100	7.9952	0.6949	1.0737	190–430

2.6 Average Boiling Point

Based on the distillation curve, different average boiling points can be estimated. Among these, the volume average boiling point (VABP) and the mean average boiling points (MeABP) are the most widely used in property estimation and design.

1- Volume Average Boiling Point (VABP)
2- Weight Average Boiling Point (WABP)
3- Molar Average Boiling Point (MABP)
4- Mean Average Boiling Points (MeABP)

1- Volume Average Boiling Point (VABP)

Given the ASTM D86 distillation, the VABP can be calculated as the average of the five boiling temperatures at 10, 30, 50, 70 and 90 volume per cent distilled (Vol.%).

$$\boxed{\text{VABP} = \frac{T_{10} + T_{30} + T_{50} + T_{70} + T_{90}}{5}} \quad \text{.......(4.3)}$$

- Where $Ti\%$ = Temp. at *i vol. %* distilled.
- where all temperatures are in (°F).
- For shortcut Boiling Point (having short B.P). $VABP = T_{50}\%$

2- Weight Average Boiling Point (WABP)

$$\boxed{WABP = \frac{T_{10\%} + T_{20\%} + T_{30\%} + \dots\dots\dots T_{90\%}}{9}} \text{..............(4.4)}$$

- $Ti\%$ = Temp. at *i* weight. % distilled
- where all temperatures are in (°F).

3- Molar Average Boiling Point (MABP)

$$MABP = \frac{Tx1+Tx2+Tx3+\cdots Txn}{x1+x2+x3+\cdots xn} \quad \text{..........(4.5)}$$

- Tix = Temp. at *i* mol. x distilled x is the no. of mole
- The relationship between the molar average boiling point (MABP) and volume average boiling point (VABP) is clear in equation (4.6)

$$\boxed{MABP = VABP + \Delta T} \quad \text{..........(4.6)}$$

- Where ΔT is estimated from Figure (5) and the Slope from equation (4.6 a)

$$\boxed{Slope = \frac{T_{70\%} - T_{10\%}}{60}} \quad \text{......................(4.6 a)}$$

If the slope < 2 ⇒ Short Cut ($T_{50\%}$) ⇒ VABP = WABP = MABP

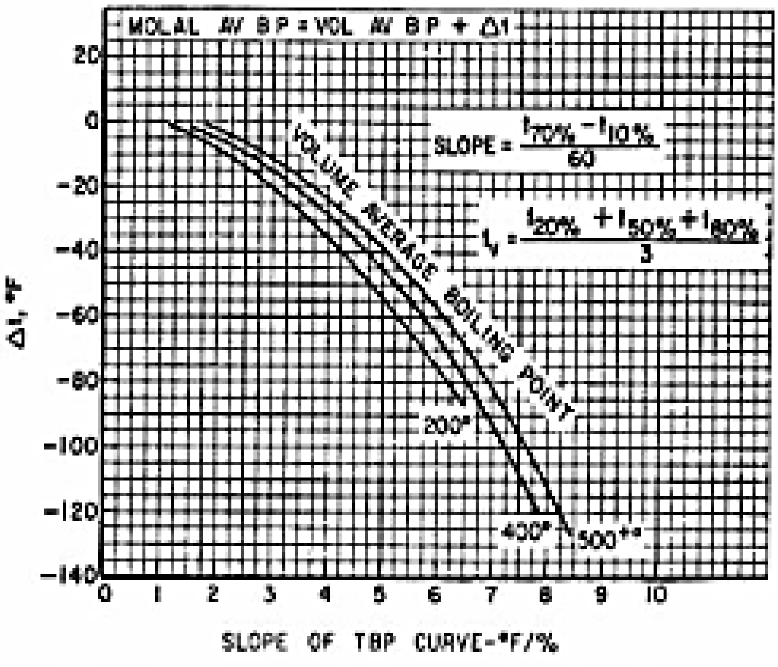


Figure 5 Molar average boiling point of petroleum fractions

4- Mean Average Boiling Points (MeABP)

The MeABP is calculated using the following equation:

$$\boxed{\mathrm{MeABP} = \mathrm{VABP} - \Delta} \quad \text{.................(4.7)}$$

Where (Δ) is the Differential in (°F) given by:

$$\boxed{\begin{gathered} \ln \Delta = -0.94402 - 0.00865(\mathrm{VABP} - 32)^{0.6667} + 2.99791\,\mathrm{SL}^{0.333} \\ \mathrm{SL} = \frac{T_{90} - T_{10}}{90 - 10} \end{gathered}} \quad \text{......(4.7a)}$$

Where SL is the slop of the VABP

- The MeABP is calculated using the slop and Figure 6:

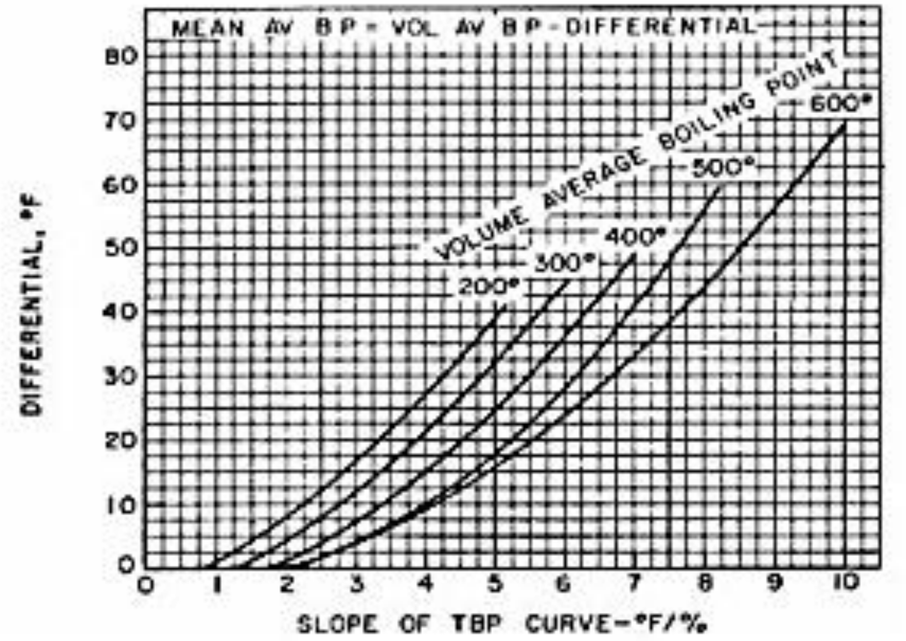


Figure 6 Mean average boiling point of petroleum fractions

Fractionation Towers

After desalting as shown in Figure 7 and 8 , the crude oil is pumped through a series of heat exchanger and its temperature raised to about 550 o F (288 o C) by heat exchange with product and reflux streams. It is then further heated to about 750 ° F (399 ° C) in a furnace (i.e. direct fired heater or "pipe still") and charged to flash zone of atmospheric fractionators.

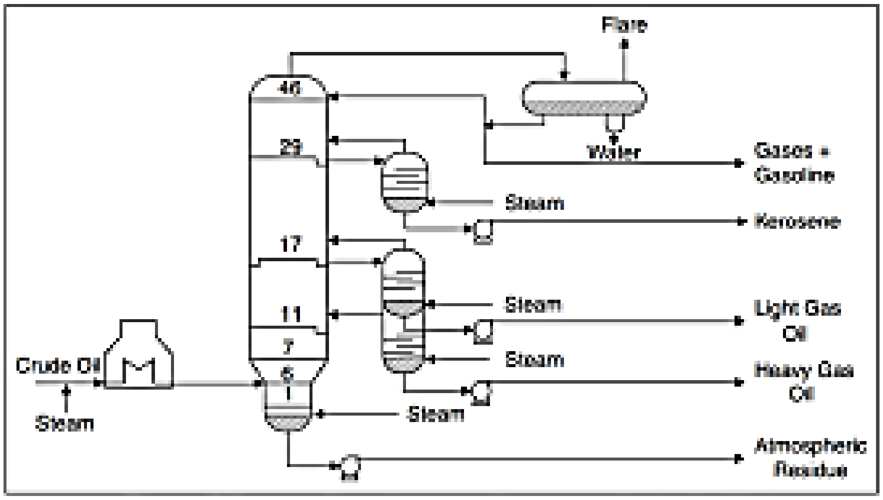


Figure 7 Process flow diagram of an atmospheric distillation unit

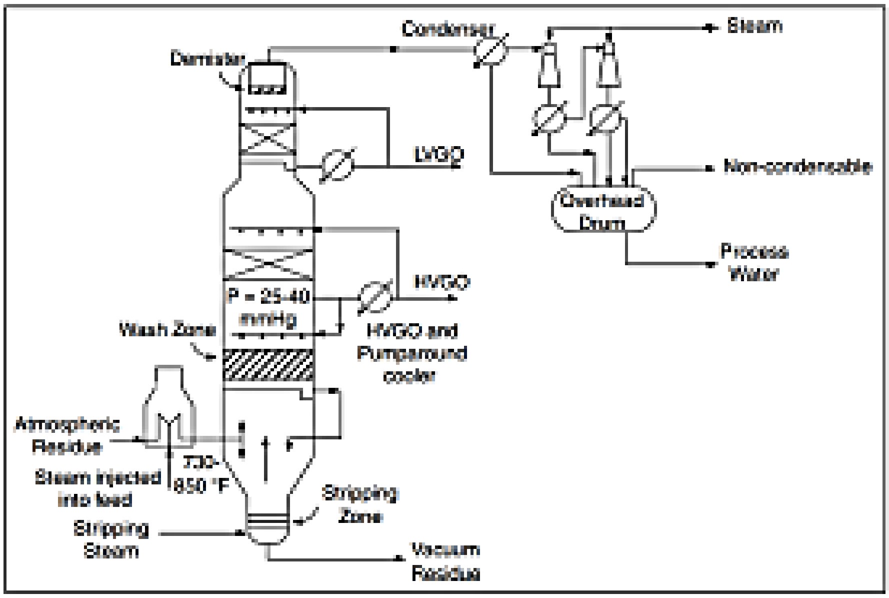


Figure 8 Process flow diagram of the vacuum distillation unit

The furnace discharge temperature is sufficiently high to cause vaporization of all products drawn above the flash zone (+ about 20%) of the bottom product. The 20 % "over flash" allows some fractionation to occur on the trays just above the flashing zone by providing internal reflux above side stream withdrawals.

In many petroleum distillations, steam is admitted to the space in which vaporization occurs, the steam reduces the partial pressure in the vapour *by Dalton's law*, and the boiling point of a material may be reduced in only two ways:

1. The pressure may be reduced.
2. Or some inert gas such as steam may be introduced.

$$P(total) = \sum_{i}^{n} Pi \quad \text{.....................(}\textit{ Dalton's law}\text{)}$$

Where *P(total): is the total pressure, Pi : is the partial pressure of gas in a mixture*

Also, the mole fraction of gases in a mixture can be calculated from this *Equation*

$$Xi = \frac{Pi}{P(total)} \quad \text{..........................(}\textit{Mole fraction}\text{)}$$

- The distillation causes the fractions to separate in increasing order of boiling point as shown in Figure 9.
- The top product being highly volatile has to be condensed in a reflux condenser, some portion of the condensed fraction goes back as reflux.
- All other fractions form the side draw products of the distillation column, these fractions are usually classified as heavy naphtha, kerosene, and gas oil.
- Bottom product of the atmospheric column is now again routed through a furnace to reach a temperature of (350 to 400° C) and is allowed to flash in a vacuum column, vacuum gas oil, heavy diesel, lubrication oil cuts/pressure distillates shall be the side cuts.

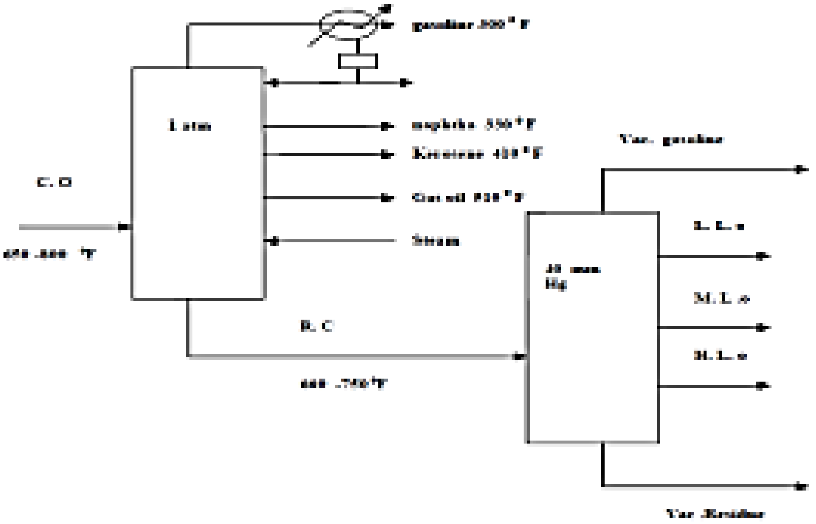


Figure 9 The fractionation process of ASTM and Vacuum distillation column

Heat and Material Balances

1. The vapour-liquid feed enters the tower at a high temperature, and the product is withdrawn at a lower temperature, hence heat must be removed, and it is referred as " **reflux heat** ".
2. The most satisfactory temperature datum is the **vaporizer temperature** because this temperature can be accurately estimated and is the temperature about which the the entire design of the tower and pipe still hinges.
3. By using this datum plane, the heat balance consists simply of the **sensible heat** required to:

a. Cool each product from vaporizer temperature to its withdrawal temperature.
b. Condense the products that are withdrawn as the liquid.

$Qs = m\,cp\,\Delta T$ ………………………………(sensible heat)

Where Qs: is sensible heat (Btu), m: is the mass flow rate of feed steam, cp: is the heat capacity and the ΔT is the difference in temperatures.
Also, to obtain the data of heat balance can be estimated **"latent heat"** from Equation:

$Ql = m\,.\lambda$ …………………………………….(latent heat)

Where Ql: is the latent heat removal (Btu), λ: is the specific latent heat of vapour during the vaporization processes.

To understand these balances reviewed **Example 3** in "The Calculation and Examples of Crude Oil Distillation".

Kinds of Reflux

Ways of removing heat are indicated in **Figure 10** below , the types of reflux:

1. Cold Reflux : is defined as reflux that is supplied at some temperature below the temperature at the top of the tower. Each pound of this reflux removes a quantity of heat equal to the its latent heat and the sensible heat required to raise it temperature from the storage tank temperature to the temperature at the top of the tower

$Q = m\lambda + m\,cp(l)\Delta T$ ………….(For cold reflux)

2. Hot Reflux :Admitted to the tower at the same temperature . Reflux or over flow from plate to plate in the tower is essentially hot reflux because it is always substantially at its boiling point. Hot reflux capable of removing only the latent heat because no difference in temperature is involved

$Q = m\lambda$……………………..(For hot reflux)

3. **Circulating Reflux** : It is not vaporized. It is only able to remove the sensible heat that is represented by its change in temperature as it circulate. This reflux is withdrawn from th tower as a liquid at a high temperature as a liquid and is returned to the tower after having been cooled.

$$Q = m\ cp(l)\Delta T \text{ ....(For circulation reflux)}$$

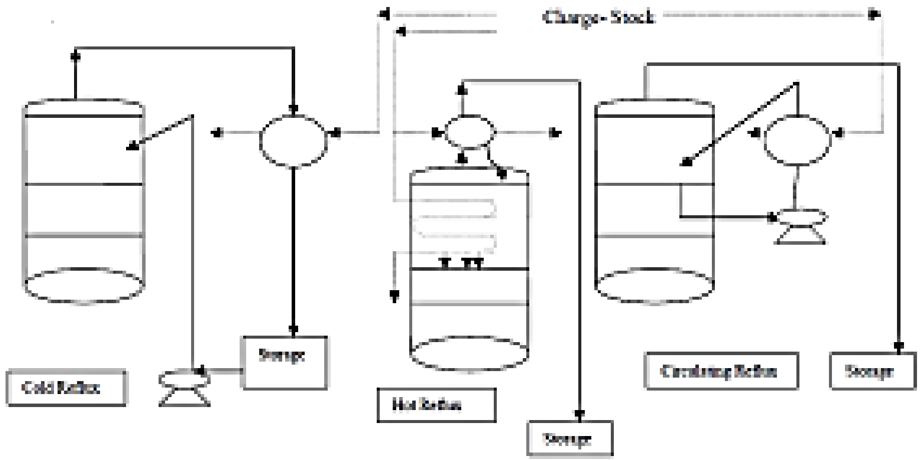


Figure 10 Type of distillation reflux