Introduction to Crude Oil and Petroleum Processing

David S. J. Jones

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David S. J. Jones: deceased.

D.S.J. Jones
Calgary, AB, Canada

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Abstract

This introduction to crude oil and petroleum processing provides a working knowledge of crude oil properties and refining to make the large array of petroleum-based products we enjoy today. Topics include the composition of crude oil, the crude assay, product properties, and the basic processes used to convert crude to useful products. This chapter sets the stage for the detailed discussions, descriptions, and calculation methods contained in the balance of this handbook.

Keywords

Refinery • Refining • Petroleum • Crude oil

Introduction

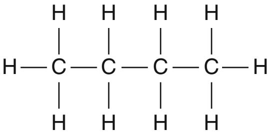
The wheel, without doubt, was man's greatest invention. However, until the late eighteenth century and early nineteenth century, the motivation and use of the wheel was limited either by muscle power, man or animal, or by energy naturally occurring from water flow and wind. The invention of the steam engine provided, for the first time, a motive power independent of muscle or the natural elements. This ignited the industrial revolution of the nineteenth century, with its feverish hunt for fossil fuels to generate the steam. It also initiated the development of the mass production of steel and other commodities.

Late in the nineteenth century came the invention of the internal combustion engine with its requirement for energy derived from crude oil. This, one can say, sparked the second industrial revolution, with the establishment of the industrial scene of today and its continuing development. The petroleum products from the crude oil used initially for the energy required by the internal combustion engine have mushroomed to become the basis and source of some of our chemical and pharmaceutical products.

The development of the crude oil refining industry and the internal combustion engine had influenced each other during the twentieth century. Other factors have also contributed to accelerate the development of both. The major factors are the increasing awareness of environmental contamination and the increasing demand for faster travel which led to the development of the aircraft industry with its need for higher-quality petroleum fuels. The purpose of this introductory chapter is to describe and define some of the basic measures and parameters used in the petroleum refining industry. These set the stage for the detailed examination of the industry as a whole which is provided in other chapters of this handbook.

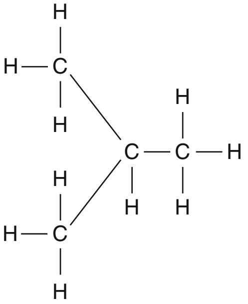
The Composition and Characteristics of Crude Oil

Crude oil is a mixture of literally hundreds of hydrocarbon compounds ranging in size from the smallest, methane, with only one carbon atom, to large compounds containing 300 and more carbon atoms. A major portion of these compounds are paraffins or isomers of paraffins. A typical example is butane shown below:



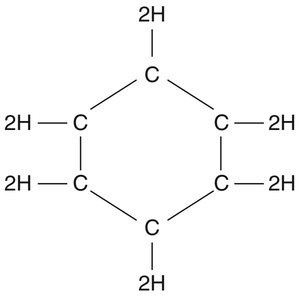
$$\mathrm{H}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\mathrm{H}$$

Normal butane(denoted as nC4)

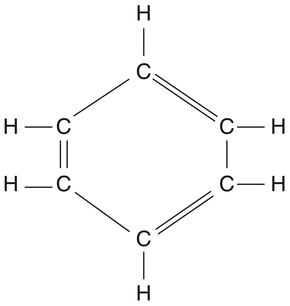


Isobutane (denoted as iC4)

Most of the remaining hydrocarbon compounds are either cyclic paraffins called naphthenes or deeply dehydrogenated cyclic compounds as in the aromatic family of hydrocarbons. Examples of these are shown below:



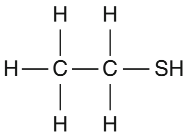
Cyclohexane (Naphthene)



Benzene (Aromatic)

Only the simplest of these homologues can be isolated to some degree of purity on a commercial scale. Generally, in refining processes, isolation of relatively pure products is restricted to those compounds lighter than C7s. The majority of hydrocarbon compounds present in crude oil have been isolated, however, but under delicate laboratory conditions. In refining processes the products are identified by groups of these hydrocarbons boiling between selected temperature ranges. Thus, for example a naphtha product would be labeled as a 90–140 °C cut.

Not all compounds contained in crude oil are hydrocarbons. There are present also as impurities small quantities of sulfur, nitrogen, and metals. By far the most important and the most common of these impurities is sulfur. This is present in the form of hydrogen sulfide and organic compounds of sulfur. These organic compounds are present through the whole boiling range of the hydrocarbons in the crude. They are similar in structure to the hydrocarbon families themselves, but with the addition of one or more sulfur atoms. The simplest of these is ethyl mercaptan which has a molecular structure as follows:



$$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{H}{\underset{H}{C}}{-}SH}$$

Ethyl Mercaptan

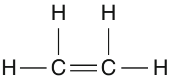
The higher carbon number ranges of these sulfur compounds are thiophenes which are found mostly in the heavy residuum range and disulfides found in the middle distillate range of the crude. The sulfur from these heavier sulfur products can only be removed by converting the sulfur to H_2S in a hydrotreating process operating under severe conditions of temperature and pressure and over a suitable catalyst. The lighter sulfur compounds can be removed as mercaptans by extraction with caustic soda or other suitable proprietary solvents or by other processes, like hydrotreating.

Organic chloride compounds are also present in crude oil. These are not removed as such but metallic protection is applied against corrosion by HCl in the primary distillation processes. This protection is in the form of Monel lining in the sections of the process most vulnerable to chloride attack. Injection of ammonia or amines is also applied to neutralize the HCl in these sections of the equipment.

The most common metal impurities found in crude oils are nickel, vanadium, and sodium. These are not very volatile and are found in the residuum or fuel oil products of the crude oil. These are not removed as metals from the crude and normally they are only a nuisance if they affect further processing of the oil or if they are a deterrent to the saleability of the fuel product. For example, the metals cause severe deterioration in the catalyst life of most catalytic processes. Also, high concentrations of nickel and vanadium are unacceptable in fuel oils used in the production of certain steels. The metals can be removed with the glutinous portion of the fuel oil product called asphaltenes. The most common process used to accomplish this is the extraction of the asphaltenes from the residue oils using propane as solvent. Coking is also common for removal of these heavy components.

Nitrogen, the remaining impurity, is usually found as dissolved gas in the crude or as amines or other nitrogen compounds in the heavier fractions. It is a problem with certain processes, such as catalytic reforming and hydrocracking. Nitrogen is removed along with the sulfur compounds by hydrotreating the feedstocks to these processes.

Although the major families or homologues of hydrocarbons found in all crude oils as described earlier are the paraffins, cyclic paraffins, and aromatics, there is a fourth group. These are the unsaturated or olefinic hydrocarbons. They are not naturally present in any great quantity in most crude oils, but are often produced in significant quantities during the processing of the crude oil to refined products. This occurs in those processes which subject the oil to high temperature for a relatively long period of time. Under these conditions the saturated hydrocarbon molecules break down, permanently losing one or more of the four atoms attached to the quadrivalent carbon. The resulting hydrocarbon molecule is unstable and readily combines with itself (forming double-bond links) or with similar molecules to form polymers. An example of such an unsaturated compound is as follows:



$$H-\overset{\overset{H}{|}}{C}=\overset{\overset{H}{|}}{C}-H$$

Ethylene

Note the double bond in this compound linking the two carbon atoms.

Although all crude oils contain the compounds described above, rarely are there two crude oils with the same characteristics. This is so because every crude oil from whatever geographical source contains different quantities of the various compounds that make up its composition. Crude oils produced in Nigeria, for example, would be high in cyclic paraffin content and have a relatively low specific gravity. Crude drilled in some of the fields in Venezuela on the other hand would have a very high specific gravity and a low content of material boiling below 350 °C. Table 1 summarizes some of the crude oils from various locations.

Worthy of note in the table is the difference in the character of the various crudes that enables refiners to improve their operation by selecting the best crude or crudes that meet their product marketing requirements. For example, where a refining product slate demands a high quantity of “no-lead” gasoline and a modest outlet for fuel oils, then a crude oil feed such as Hassi Messaoud would be a prime choice. Its selection provides a high naphtha yield with a high naphthene content as catalytic reforming feedstock. Fuel oil in this case also is less than 50 % of the barrel. The Iranian light crude would also be a contender but for the undesirably high metal content of the fuel oil (residuum).

In the case of a good middle of the road crude, Kuwait or the Arabian crude oils offer a reasonably balanced product slate with good middle distillate quality and yields.

For bitumen manufacture and lube oil manufacture, the South American crude oils are formidable competitors. Both major crudes from this area, Bachequero, the heavier crude, and Tia Juana, the lighter, are highly acidic (naphthenic acids) which enhances bitumen and lube oil qualities. There is a problem with these crude oils however as naphthenic acids are very corrosive in atmospheric distillation columns, particularly in the middle distillate sections. Normal distillation units may require relining of sections of the tower with 410 stainless steel and/or injection of caustic if extended processing of these crude oils is envisaged.

Refiners often mix selected crude oils to optimize a product slate that has been programmed for the refinery. This exercise requires careful examination of the various crude assays (data compilation) and modeling the refinery operation to set the crude oil mix and its operating parameters.

The Crude Oil Assay

The crude oil assay is a compilation of laboratory and pilot plant data that define the properties of the specific crude oil. At a minimum, the assay should contain a distillation curve for the crude and a specific gravity curve. Most assays however contain data on pour point (flowing criteria), sulfur content, viscosity, and many other properties. The assay is usually prepared by the company selling the crude oil; it is used extensively by refiners in their plant operation, development of product schedules, and examination of future processing ventures. Engineering companies

Table 1 Characteristics of some crude oils from various worldwide locations

	Arabian light	Arabian heavy	Iranian light	Iranian heavy (Gach Saran)	Iraq (Kirkuk)	Kuwait	Algerian (Hassi Messaoud)	Libyan (Brega)	Nigerian (Bonny medium)	North Sea (Ekofisk)	South American (Bachequero)
% vol. boiling below 350 °C	54.0	46.5	55.0	53.0	61.1	49.0	75.2	64.0	54.5	61.2	30.0
Gravity, API	33.4	28.2	33.5	30.8	35.9	31.2	44.7	40.4	26.0	36.3	16.8
Sulfur, wt%	1.8	2.84	1.4	1.6	1.95	2.5	0.13	0.21	0.23	0.21	2.4
PONA of heavy naphtha, vol%											
Cut, °C	100–150	100–150	149–204	149–204	100–150	100–150	95–175	100–150	100–150	100–200	93–177
Paraffins	69.5	70.3	54.0	50	69.0	67.9	56.5	53.0	27.5	56.5	27.6
Olefins	–	–	–	–	265 ppm	–	–	20 ppm	1.5	–	–
Naphthenes	18.2	21.4	30.0	35	21.0	22.1	32.9	39.3	57.0	29.5	58.5
Aromatics	12.3	8.3	16.0	15	9.8	10.0	10.6	7.7	14.0	14.0	13.9
Metals in residuum											
Residuum temp. °C	>565	>565	>538	>538	>370	>370	>350	>570	>535	>350	>350
Vanadium, wt ppm	94	171	188	404	58	59	<5	24	7	1.95	437
Nickel, wt ppm	22	53	70	138	<3	18	<5	32	52	5.04	75

The Bachequero pour point is 16 °C

use the assay data in preparing the process design of petroleum plants they are bidding on or, having been awarded the project, they are now building.

In order to utilize the crude oil assay, it is necessary to understand the data it provides and the significance of some of the laboratory tests that are used in its compilation. Some of these are summarized below and are further described and discussed in other chapters of the handbook.

The True Boiling Point Curve

This is a plot of the boiling points of almost pure components, contained in the crude oil or fractions of the crude oil. In earlier times this curve was produced in the laboratory using complex batch distillation apparatus of a hundred or more equilibrium stages and a very high reflux ratio. Nowadays, this curve is produced by mass spectrometry techniques much quicker and more accurately than by batch distillation. A typical true boiling point curve (TBP) is shown in Fig. 10.

The ASTM Distillation Curve

While the TBP curve is not produced, on a routine basis the ASTM distillation curves are. Rarely, however, is an ASTM curve conducted on the whole crude. This type of distillation curve is used on a routine basis for plant and product quality control. This test is carried out on crude oil fractions using a simple apparatus designed to boil the test liquid and to condense the vapors as they are produced. Vapor temperatures are noted as the distillation proceeds and are plotted against the distillate recovered. Because only one equilibrium stage is used and no reflux is returned, the separation of components is poor. Thus, the initial boiling point (IBP) for ASTM is higher than the corresponding TBP point and the final boiling point (FBP) of the ASTM is lower than that for the TBP curve. There is a correlation between the ASTM and the TBP curve, and this is dealt with later in this chapter.

API Gravity

This is an expression of the density of an oil. Unless stated otherwise the API gravity refers to density at 60 °F (15.6 °C). Its relationship with specific gravity is given by the following expression:

$$\text{API}^\circ = \frac{141.5}{\text{sp.gr.}} - 131.5 \tag{1}$$

Flash Points

The flash point of an oil is the temperature at which the vapor above the oil will momentarily flash or explode. This temperature is determined by laboratory testing using an apparatus consisting of a closed cup containing the oil, heating and stirring equipment, and a special adjustable flame. The type of apparatus used for middle distillate and fuel oils is called the Pensky-Martens (PM), while the apparatus used in the case of kerosene and lighter distillates is called the Abel. References to these tests are given later in this handbook, and full details of the test methods and procedures are given in ASTM Standards Part 7, Petroleum Products and Lubricants. There are many empirical methods for determining flash points from the ASTM distillation curve. One such correlation is given by the following expression:

$$\text{Flash point } {}^{\circ}\text{F} = 0.77(\text{ASTM } 5\ \%\ {}^{\circ}\text{F} - 150\,{}^{\circ}\text{F}) \tag{2}$$

Octane Numbers

Octane numbers are a measure of a gasoline resistance to knock or premature detonation in a cylinder of a gasoline engine. The higher this resistance, the higher will be the efficiency of the fuel to produce work. A relationship exists between the antiknock characteristic of the gasoline (octane number) and the compression ratio of the engine in which it is to be used. The higher the octane rating of the fuel, the higher the compression ratio of the engine in which it can be used.

By definition, an octane number is that percentage of isooctane in a blend of isooctane (2,2,4-trimethylpentane) and normal heptane that exactly matches the knock behavior of the gasoline. Thus, a 90 octane gasoline matches the knock characteristic of a blend containing 90 % isooctane and 10 % *n*-heptane. The knock characteristics are determined in the laboratory using a standard single cylinder test engine equipped with a super sensitive knock meter. The reference fuel (isooctane blend) is run and compared with a second run using the gasoline sample. Details of this method are given in the ASTM Standards Part 7, Petroleum Products and Lubricants.

Two octane numbers are usually determined. The first is the research octane number (ON res or RON) and the second is the motor octane number (ON mm or MON). The same basic equipment is used to determine both octane numbers, but the engine speed for the motor method is much higher than that used to determine the research number. The actual octane number obtained in a commercial vehicle would be somewhere between these two. The significance of these two octane numbers is to evaluate the sensitivity of the gasoline to the severity of operating conditions in the engine. The research octane number is usually higher than the motor number; the difference between them is termed the “sensitivity of the gasoline.”

Viscosity

The viscosity of an oil is a measure of its resistance to internal flow and is an indication of its lubricating qualities. In the oil industry it is usual to quote viscosities either in centistokes (which is the unit for kinematic viscosity), Saybolt universal seconds, Saybolt Furol seconds, or Redwood seconds. These units have been correlated and such correlations can be found in most data books. In the laboratory, test data on viscosities is usually determined at temperatures of 100 °F, 130 °F, or 210 °F. In the case of fuel oils, temperatures of 122 °F and 210 °F are used.

Cloud and Pour Points

Cloud and pour points are tests that indicate the relative coagulation of wax in the oil. They do not measure the actual wax content of the oil. In these tests, the oil is reduced in temperature under strict control using an ice bath initially and then a frozen brine bath and finally a bath of dry ice (solid CO_2). The temperature at which the oil becomes hazy or cloudy is taken as its cloud point. The temperature at which the oil ceases to flow altogether is its pour point.

Sulfur Content

This is self-explanatory and is usually quoted as %wt or wt ppm (wppm) for the total sulfur in the oil.

Assays change in the data they provide as the oils from the various fields change with age. Some of these changes may be quite significant and users usually request updated data for definitive work, such as process design or evaluation. The larger producers of crude oils provide laboratory test services on an “ongoing” basis for these users.

The next few sections of this chapter illustrate how the assay data and basic petroleum refining processes are used to develop a process configuration for an oil refining complex.

Other Basic Definitions and Correlations

As described earlier, the compositions of crude oil and its fractions are not expressed in terms of pure components, but as “cuts” expressed between a range of boiling points. These “cuts” are further defined by splitting them into smaller sections and treating those sections as though they were pure components. As such, each of these components will have precise properties such as specific gravity, viscosity, mole weight, pour point, etc. These components are referred to as pseudo components and are defined in terms of their mid-boiling point.

Before describing in detail the determination of pseudo components and their application in the prediction of the properties of crude oil fractions, it is necessary to define some of the terms used in the crude oil analysis. These are as follows:

Bubble Point

Bubble point is the temperature and pressure at which a hydrocarbon begins to boil. An example of bubble point calculation for a stream is provided here as an example. The bubble point can also be calculated using process simulation software (HYSYS, Pro/II, or other programs) with selection of appropriate thermodynamic/equilibrium systems. Understanding the manual calculation approach is useful in interpreting and evaluating the computer calculation results.

Consider an overhead stream from a fractionator that has the following composition:

Mole fraction composition:

C_2	0.008
C_3	0.054
iC_4	0.021
nC_4	0.084
C_5s	0.143
C_6	0.155
C_7	0.175
Comp 1	0.124
Comp 2	0.124
Comp 3	0.075
Comp 4	0.037
Total	1.00

The components 1–4 are pseudo components that have properties similar to real components with the same boiling point. These pseudo components are discussed more below. The mid-boiling points of the components are taken as:

	°F
Comp 1	260
Comp 2	300
Comp 3	340
Comp 4	382

The reflux drum temperature will be fixed at 100 °F. You want to determine the pressure for the reflux drum at ***the bubble point*** of this material at 100 °F.

Now, at the bubble point, the sum of all y's = sum of all Kx's.

x is the mole fraction of a component in the liquid phase and y is the mole fraction of the component in the vapor phase at equilibrium. At bubble point $\Sigma y = \Sigma Kx$.

K is the equilibrium constant and can be read from the curves found in textbooks such as Maxwell's *Data Book on Hydrocarbons* or can be considered (rough and not be used for definitive design) as

$$K = \text{Vapor Pressure(at temperature)/Total Pressure} \tag{3}$$

This relationship will be used for this calculation. The calculation is iterative (trial and error) as follows (at 100 °F):

		1st Trial at 5 psig		2nd Trial at 12 psig	
	Mol fract. X	K	$Y = KX$	K	$Y = KX$
C_2	0.008	40.6	0.325	32.4	0.259
C_3	0.054	9.3	0.502	7.42	0.401
iC_4	0.021	3.55	0.075	2.38	0.05
nC_4	0.084	2.54	0.213	2.03	0.171
C_5	0.143	0.89	0.127	0.71	0.102
C_6	0.155	0.254	0.039	0.20	0.031
C_7	0.175	0.084	0.015	0.067	0.011
Comp 1	0.124	0.023	0.003	0.020	0.002
Comp 2	0.124	NEG	NEG		
Comp 3	0.075	NEG	NEG		
Comp 4	0.037	NEG	NEG		
	1.000		1.299		1.027

For second trial (estimate)

Take the K value of the highest fraction of y (in this case C3) where $K = 9.3$.

Take this $K = 7.42$ (new K).

Make the second trial with K_{C3} at 7.42 which gives a systems pressure P as follows: VP $C_3 = 7.1$ where VP C3 at 100 °F is 190 psia.

Then P = 190/7.1 = 26.5 psia.

Second trial pressure = 26.5 psia = 11.8 psig. Let's set it at 12 psig.

The second trial gives sum of Y's = 1.027 and this is considered close enough to 1.000. Then the drum will be operated at 100 °F and at 12 psig.

Cut Point

A cut point is defined as that temperature on the whole crude TBP curve that represents the limits (upper and lower) of a fraction to be produced. Consider the curve shown in Fig. 1 of a typical crude oil TBP curve.

A fraction with an upper cut point of 100 °F produces a yield of 20 % volume of the whole crude as that fraction. The next adjacent fraction has a lower cut point of 100 °F and an upper one of 200 °F; this represents a yield of 30–20 % = 10 % volume on crude.

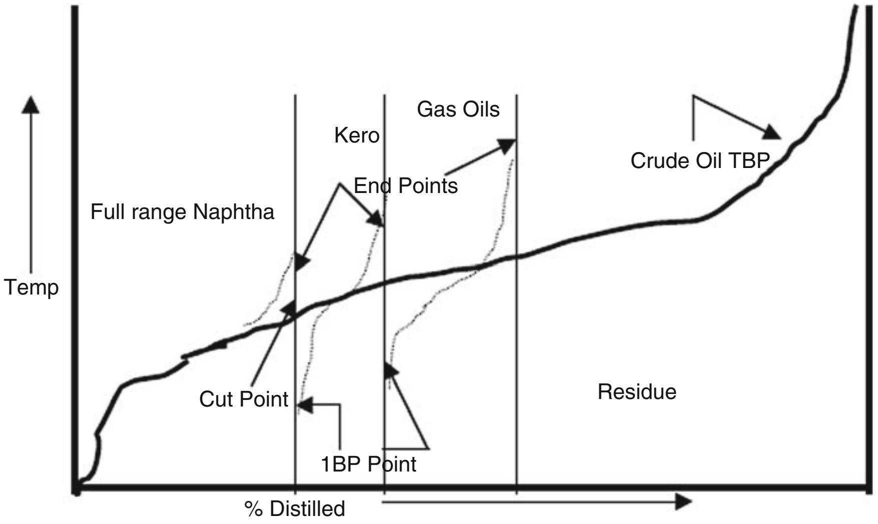


Fig. 1 Cut points and end points

End Points

While the cut point is an ideal temperature used to define the yield of a fraction, the end points are the actual terminal temperatures of a fraction produced commercially. No process has the capability to separate perfectly the components of one fraction from adjacent ones. When two fractions are separated in a commercial process, some of the lighter components remain in the adjacent lighter fraction. Likewise some of the heavier components in the fraction find their way into the adjacent heavier fraction. Thus, the actual IBP of the fraction will be lower than the initial cut point, and its FBP will be higher than the corresponding final cut point. This is also shown in Fig. 1.

Mid-boiling Point Components

In compiling the assay narrow boiling fractions are distilled from the crude and are analyzed to determine their properties. These are then plotted against the mid-boiling point of these fractions to produce a smooth correlation curve. To apply these curves for a particular calculation, it is necessary to divide the TBP curve of the crude, or fractions of the crude, into mid-boiling point components. To do this, consider Fig. 2. For the first component take an arbitrary temperature point A. Draw a horizontal line through this from the 0 % volume. Extend the line until the area between the line and the curve on both sides of the temperature point A are equal. The length of the horizontal line measures the yield of component

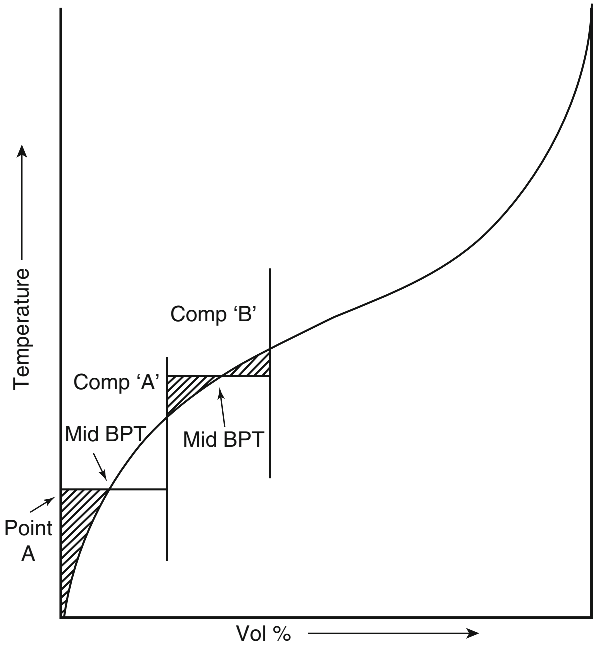


Fig. 2 Example of mid-boiling points

A having a mid-boiling point A °F. Repeat for the next adjacent component and continue until the whole curve is divided into these mid-boiling point components.

Mid-volume Percentage Point Components

Sometimes the assay has been so constructed as to correlate the crude oil properties against components on a mid-volume percentage basis. In using such data as this, the TBP curve is divided into mid-volume point components. This is easier than the mid -boiling point concept and requires only that the curve be divided into a number of volumetric sections. The mid-volume figure for each of these sections is merely the arithmetic mean of the volume range of each component.

Using these definitions the determination of the product properties can proceed using the distillation curves for the products, the pseudo component concept, and the assay data. This is given in the following discussion.

Predicting TBP and ASTM Curves from Assay Data

The properties of products can be predicted by constructing mid-boiling point components from a TBP curve and assigning the properties to each of these components.

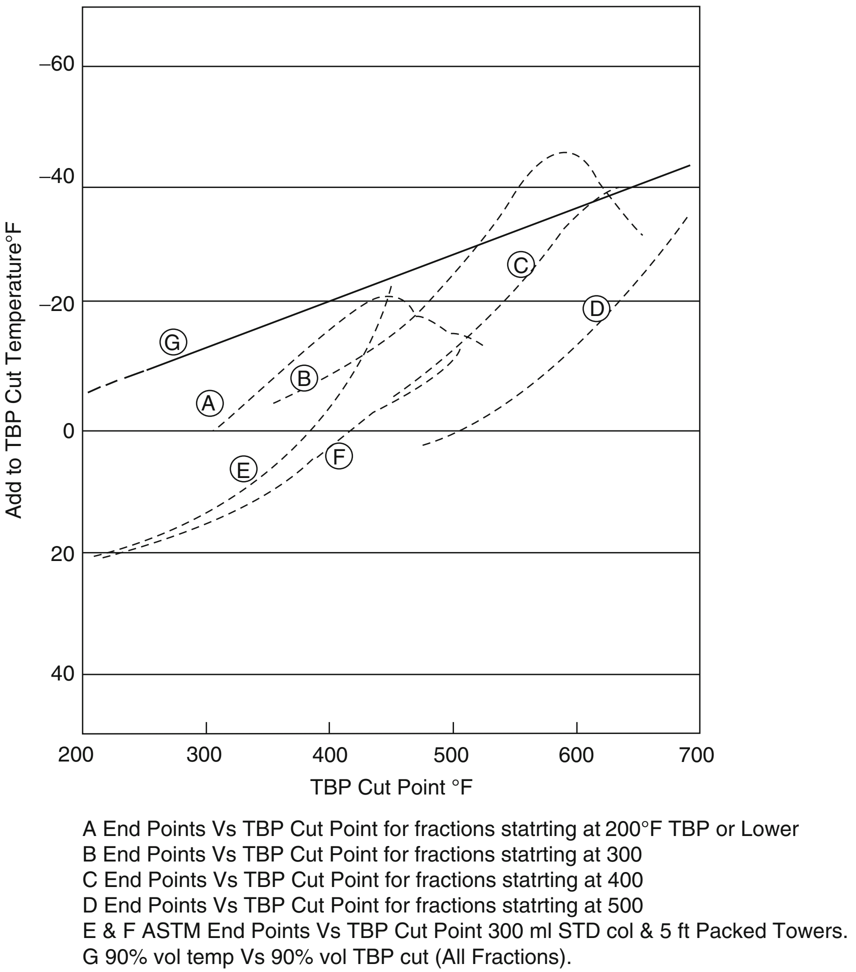


Fig. 3 Correlation between TBP and ASTM end points

These assigned properties are obtained either from the assay data, known components of similar boiling points, or established relationships such as gravity, molecular weights, and boiling points. However, before these mid-boiling points (pseudo) components can be developed, it is necessary to know the shape of the product TBP curve. The following is a method by which this can be achieved. Good et al. (1944) accumulated data to relate the ASTM end point to a TBP cut point over the light and middle distillate range of crude. Their correlation curves are given in Fig. 3 and are self-explanatory. Thrift (1961) derived a probable shape of ASTM data. The probability graph that he developed is given in Fig. 4. The product ASTM curve from a well-designed unit would be a straight line from 0 % vol to 100 % vol

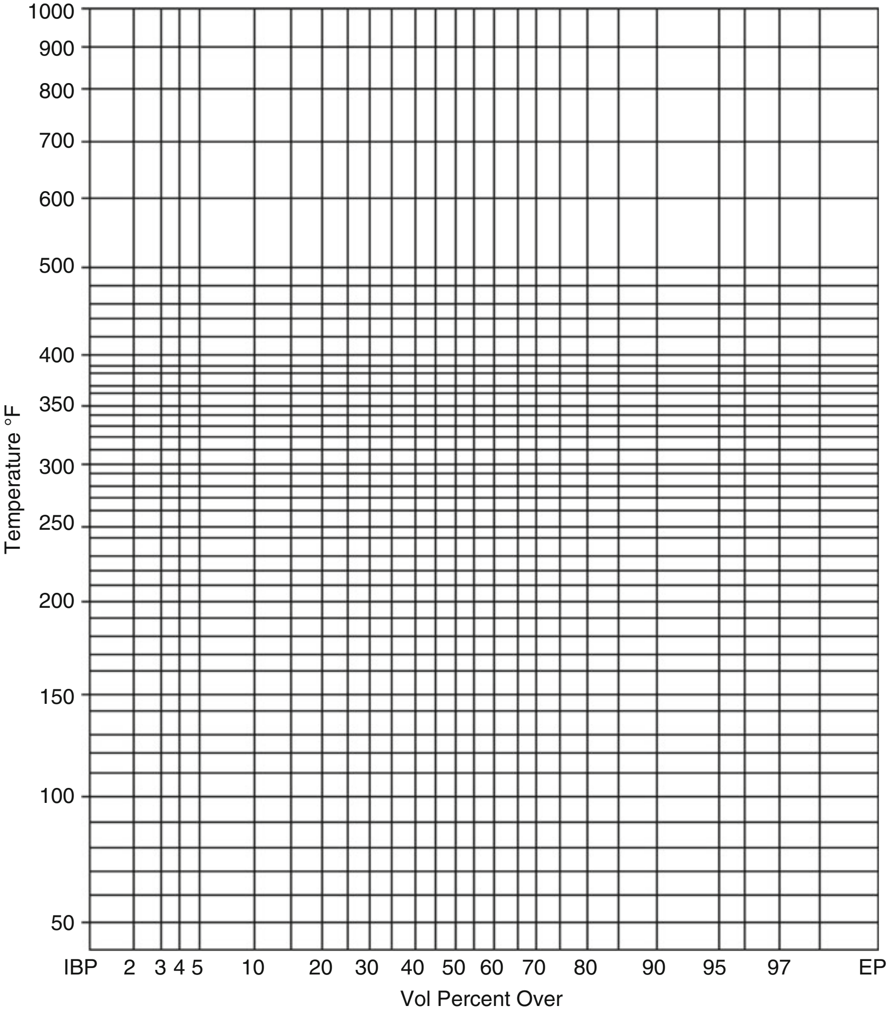


Fig. 4 ASTM distillation probability curves

on this graph. Using these two graphs it is possible now to predict the ASTM distillation curve of a product knowing only its TBP cut range.

An example of this calculation is given below:

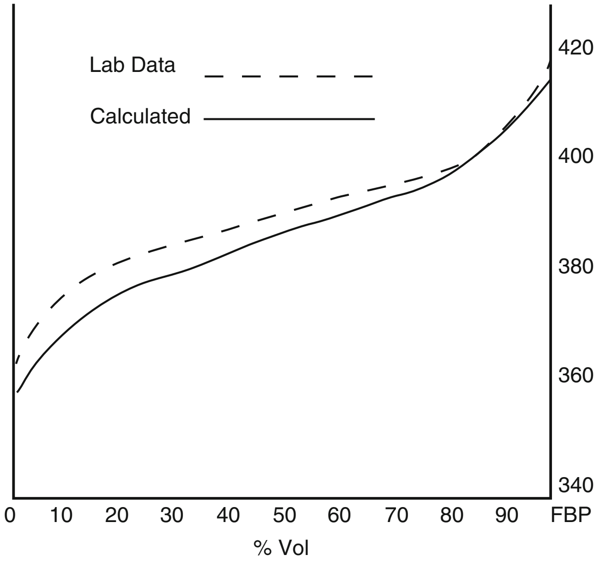
It is required to predict the ASTM distillation curve for kerosene, cut between 387 and 432 °F cut points on Kuwait crude.

Solution Yield on crude = 3.9 % vol

Cut range = 27.3–31.2 % vol on crude.

Ninety percent vol of cut = 30.81 which is = 430 °F

Fig. 5 Comparison between calculated ASTM curve and lab data



From Fig. 3, curve B ASTM end point = 432–13 °F = 419 °F

From Fig. 3, curve G ASTM 90 % point = 430–24 °F = 406 °F

These two points are plotted in Fig. 4 and a straight line drawn through them to define the probable ASTM distillation of the cut. This is plotted linearly in Fig. 5 and can be seen to compare well with laboratory results of the actual product from a crude distillation unit.

Developing the TBP Curve and the Equilibrium Flash Vaporization (EFV) Curve from the ASTM Distillation Curve

Using a product ASTM distillation curve developed as shown above, the TBP curve is developed as follows:

Converting the Product ASTM Distillation to TBP

Most crude distillation units take a full-range naphtha cut as the overhead product. This cut contains all the light ends, ethane through pentanes, in the crude and of course the heavier naphtha cut. All the light ends are in solution; therefore, it is not possible to prepare a meaningful ASTM distillation on this material directly. Two routes can be adopted in this case: the first is to take naphtha samples of the heavy naphtha and debutanized light naphtha from downstream units. Alternatively the sample can be subject to light end analysis in the lab such as using POD apparatus (Podbielniak), a gas chromatograph, or and carrying out an ASTM distillation on the stabilized sample. It is the third route that is chosen for this case.

There are two well-proven methods for this conversion. The first is by Edmister and given in his book *Applied Hydrocarbon Thermodynamics* and the second by

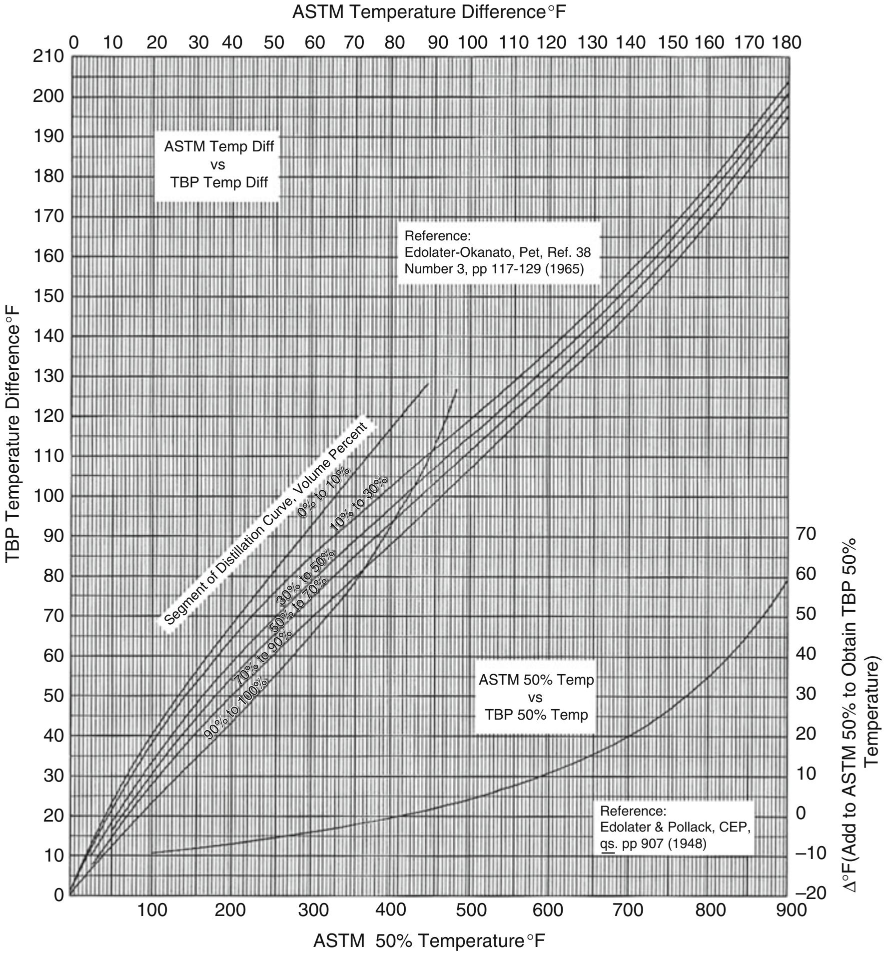
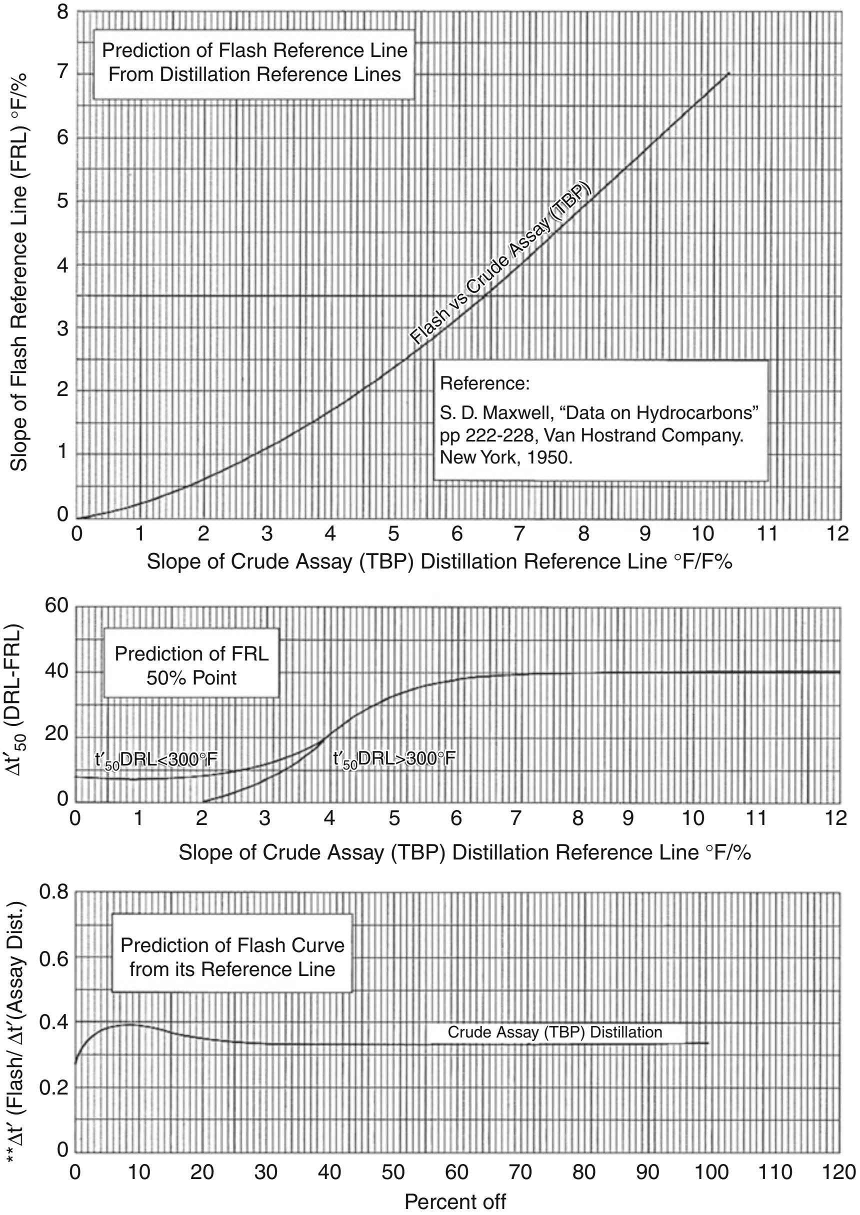


Fig. 6 ASTM–TBP correlation – Edmister method

Maxwell (1968) in his book *Data Book on Hydrocarbons*. The correlation curves from both these sources are given as Figs. 6 and 7. In this exercise Edmister's method and correlation will be used.

The ASTM distillation is tabulated as the temperature for IBP, 10 %, 20 %, through to the FBP. IBP is the initial boiling point (equivalent to 0 % over) and the FBP is the final boiling point (equivalent to 100 % vol over). The multiples of 10 % reflect the volume distilled and the temperature at which each increment is distilled. Using Fig. 6, the 50 % vol TBP point (in degrees Fahrenheit) is calculated from the 50 % vol point of the ASTM distillation.

Figure 6 is then used to determine the TBP temperature difference from the ASTM temperature difference for the 0–10 % vol, 10–30 % vol, 30–50 % vol, 50–70 % vol, 70–90 % vol, and 90–100 % vol. Moving from the established 50 % vol TBP figure



NOTE: * Flash and distillation reference lines (FRL and DRL) are straight lines through the 10% and 70% points. The temperature of the 50% points refer to these reference lines.

** $\Delta t'$ is the departure of the actual flash and distillation curves from their respective reference lines. While the individual ($\Delta t'$)'s may be either plus or minus, the ratio is always positive.

Fig. 7 EFV–TBP correlation – Maxwell method

Table 2 Converting ASTM to TBP distillation

	ASTM (lab data)		TBP (from Fig. 6)	
	°F	Δ°F	Δ°F	°F
IBP	424	29	61	361
10 %vol	453	31	52	423
30 %vol	484	18	52	475
50 %vol	502			507
70 %vol	504	2	31	538
90 %vol	536	32	41	579
FBP	570	34	40	619

and using the temperature differences given by Fig. 6, the TBP temperatures at 0 %, 10 %, 30 %, 50 %, 70 %, 90 %, and 100 % vol are obtained (Table 2).

Developing the Equilibrium Flash Vaporization Curve (EFV)

The Maxwell curves given as Fig. 7 are used to develop the equilibrium flash vaporization curve (EFV) from the TBP. The EFV curve gives the temperature at which a required volume of distillate will be vaporized. This distillate vapor is always in equilibrium with its liquid residue. The development of the EFV curve is always at atmospheric pressure. Other temperature- and pressure-related conditions may be determined by using the vapor pressure curves or by constructing a phase diagram.

The TBP reference line (DRL) is first drawn by a straight line through the 10 % vol point and the 70 % vol point on the TBP curve. The slope of this line is determined as temperature difference per volume percent. These data are then used to determine the 50 % volume temperature of a flash reference line (FRL). The curve in Fig. 7 relating Δt_{50} (DRL–FRL) to DRL slope is used for this. Finally, the curve on Fig. 7 relating the ratio of temperature differences between the FRL and flash curve (EFV) from that for the TBP to DRL is applied to each percent volume. From this the atmospheric EFV curve is drawn.

A sample calculation for the compilation of the EFV curve follows. Note that the TBP curve is used to define product yields, while the EFV curve is used to define temperature/pressure conditions in distillation. This example uses the TBP curve developed above as a starting point (Table 3).

Calculating Vapor and Liquid Compositions from Equilibrium Flash

When a mixture of compounds vaporizes or condenses, there is a unique relationship between the composition of the mixture in the liquid phase and that in the corresponding phase at any condition of temperature and pressure. This relationship is termed the equilibrium flash vaporization for the mixture. An equilibrium flash can be calculated using the procedure detailed in Appendix 1 of the current chapter.

Today these calculations are normally performed using process simulation software; however, the principles are the same as the manual calculation method.

Table 3 Converting TBP to EFV distillation

% Volume	Δt (TBP – DRL), °F	ΔT (Flash FRL)/ ΔT (TBP–DRL)	Δt (Flash–FRL), °F	Flash, °F
0	−46	0.2	−9.2	453
10	0	0.4	0	469
20	9	0.38	3.4	482
30	14	0.37	5.2	491
40	13	0.37	4.8	498
50	7	0.37	2.6	507
60	4	0.37	1.5	511
70	0	0.37	0	514
80	−2	0.37	−0.8	523
90	0	0.37	0	531
100	22	0.37	8.1	547

The resulting TBP curves and EFV curves are shown in Fig. 8

Flash calculations are among the most common calculations required to design and analyze petroleum processing operations.

Predicting Product Qualities

The following paragraphs describe the prediction of product properties using pseudo components (mid-boiling point) and assay data. A diesel cut with TBP cut points 432–595 °F on Kuwait crude (Fig. 9) will be used to illustrate these calculations. The actual TBP of this cut is predicted using the method already described. The curve is then divided into about six pseudo mid-boiling point components as described earlier and is shown in Fig. 10.

Predicting the Gravity of the Product

Using the mid-boiling point versus specific gravity curve from the assay given in Appendix C of this handbook, the SG for each component is obtained. The weight factor for each component is then obtained by multiplying the volume percent of that component *by the specific gravity. The sum of the weight factors divided by the 100 % volume* total is the specific gravity of the gas oil cut. This is shown in Table 4.

The Prediction of Product Sulfur Content

The prediction of sulfur content is similar to the method used for gravity. First the TBP curve for the product is determined and split into pseudo boiling

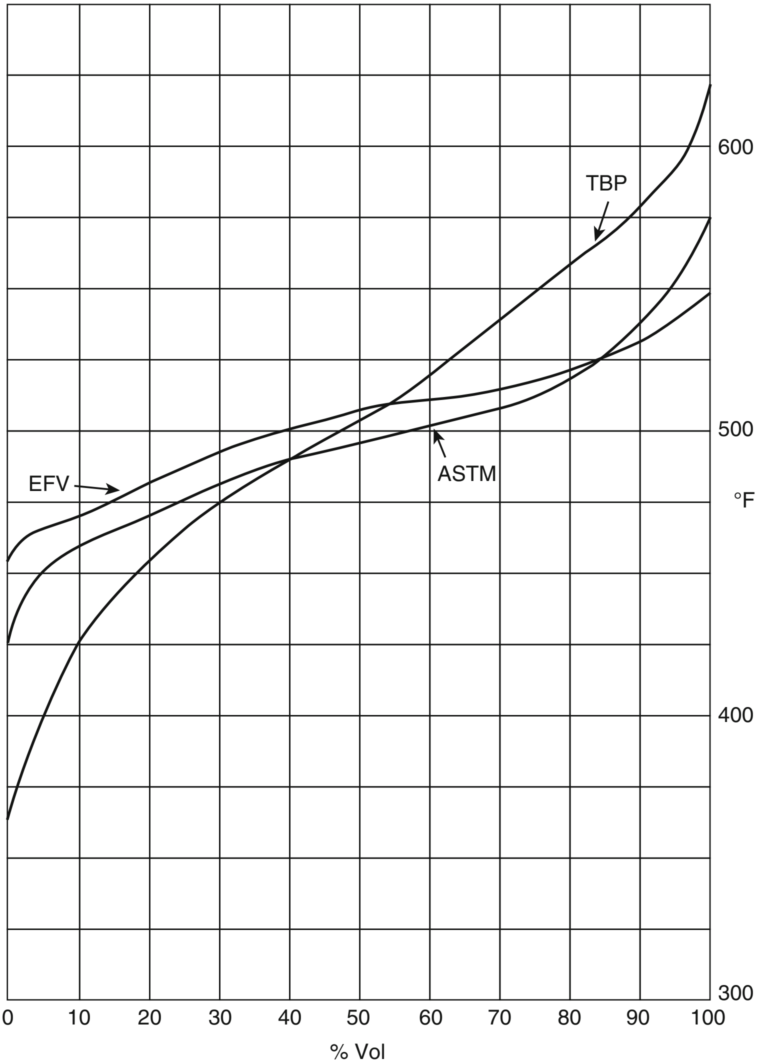


Fig. 8 Types of distillation curves

point components. The weight factor is then determined for each component as before. Note that sulfur content is always quoted as a percent weight. Using the relationship of percent sulfur to mid-boiling point given in the assay, the sulfur content of each component is read off. This is multiplied by the weight factor for each component to give a sulfur factor. The sum of the total sulfur factors divided by the total weight factor gives the weight percent sulfur content of the fraction. For example, using the same gas oil cut as before, its sulfur content is determined as shown in Table 5.

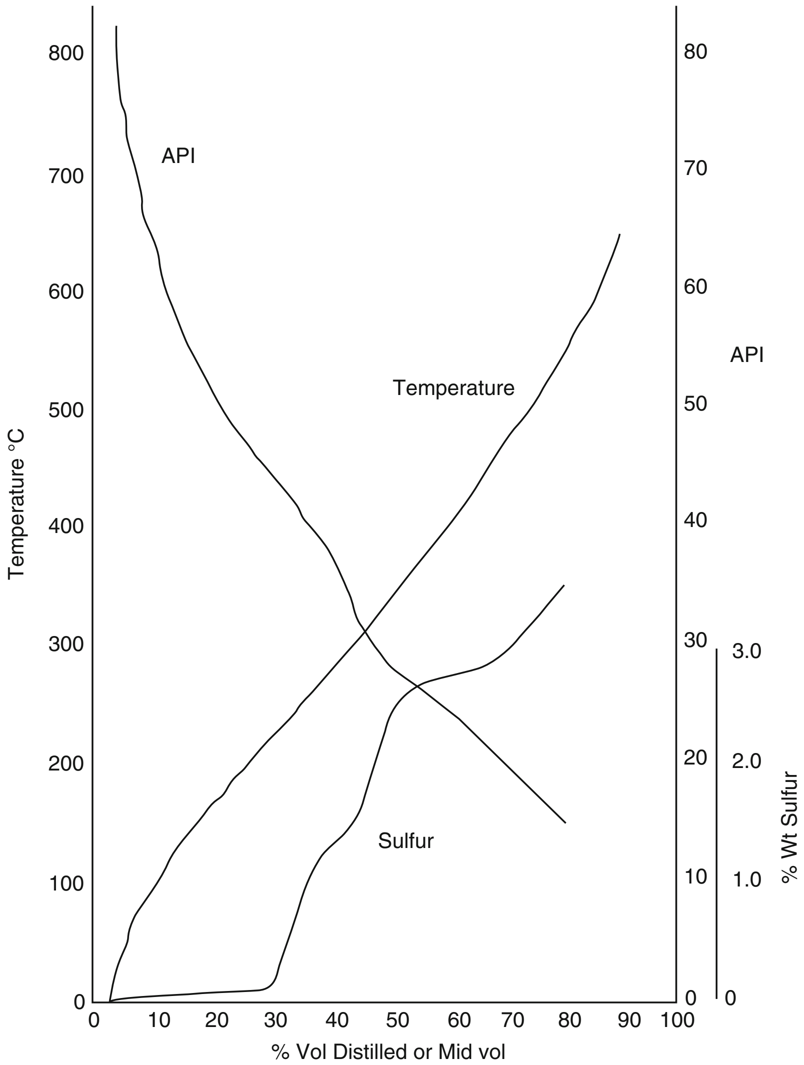


Fig. 9 Typical crude assay curves (based on Kuwait crude)

Viscosity Prediction from the Crude Assay

Unlike sulfur content and gravity, viscosity cannot be arithmetically related directly to components. To determine the viscosity of a blend of two or more components, a blending index must be used. A graph of these indices is given in Maxwell's *Data Book on Hydrocarbons*, and part of this graph is reproduced in Fig. 11. Using the blending indices and having divided the TBP curve into components as before, the viscosity of the fraction can be predicted as shown in Table 6.

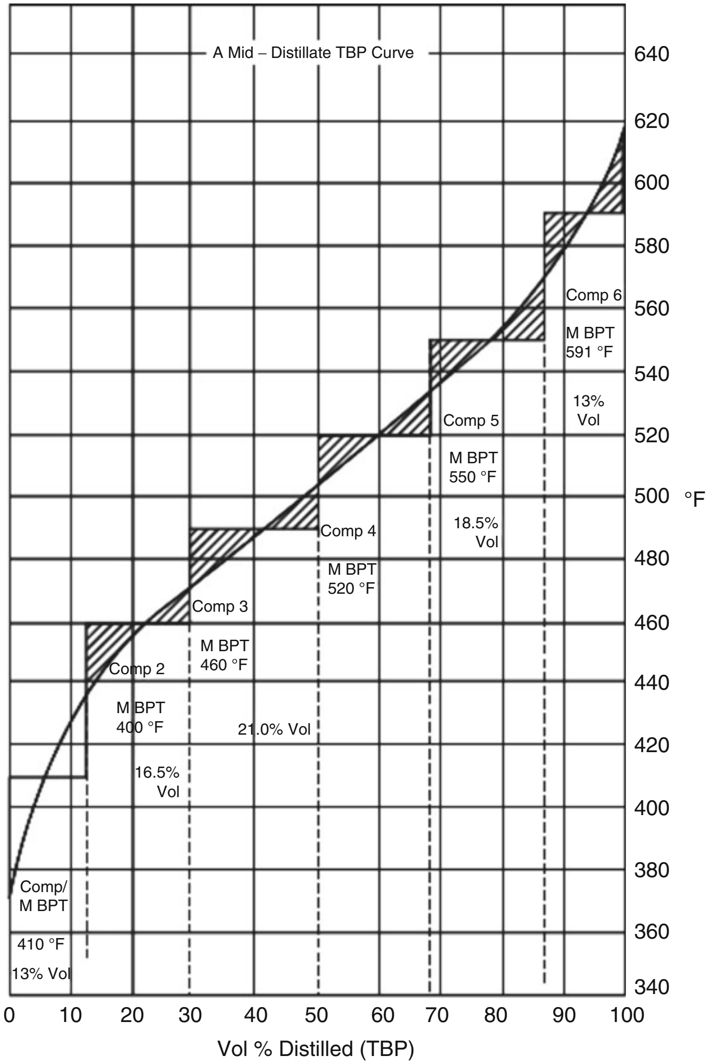


Fig. 10 Typical pseudo component breakdown

Cloud and Pour Points

In predicting these properties, it is not necessary to break down the product TBP as we have done for specific gravity, sulfur, etc. The accuracy of the tests and of blending indices does not warrant this. These properties are therefore read off directly from the mid-boiling point of the whole product. Considering the gas oil used in the previous example, its mid-boiling point is about 510 °F, from the crude assay its pour point is −5 °F, and cloud point is +4 °F. Determining pour point for a blend of two or more products is rather more difficult. In this case blending indices

Table 4 Calculating the SG of a cut

Component	Volume %	Mid-BPt, °F	SG at 60 °F	Weight factor
1	13.0	410	0.793	10.3
2	16.5	460	0.801	13.2
3	21.0	489	0.836	17.6
4	18.0	520	0.844	15.2
5	18.5	550	0.846	15.7
6	13.0	592	0.850	11.1
Total	100.0			83.1

$\text{SG of cut} = \frac{83.1}{100} = 0.831$

Table 5 Calculating the sulfur content of a cut

Component	Weight factor	Mid-BPt, °F	Sulfur, % wt	Sulfur factor
1	10.3	410	0.2	2.06
2	13.2	460	0.41	5.41
3	17.6	489	0.84	14.78
4	15.2	520	1.16	17.63
5	15.7	550	1.35	21.2
6	11.1	592	1.5	16.65
Total	83.1			77.73

$\text{Sulfur \% weight} = \frac{77.7}{83.1} \times 100 = 0.935\,\%\text{wt. (actual plant data gave } 0.931\,\%\text{wt.)}$

are used for this purpose. A graph of these indices is given in Fig. 12. It is self-explanatory and its application is explained in Table 7.

Flash Points

The flash point of a product is related to its ASTM distillation by the expression:

$$\text{Flash point} = 0.77(\text{ASTM } 5\,\% \text{ in } ^\circ\text{F} - 150\,^\circ\text{F}) \qquad (4)$$

Thus, for the gas oil product in the above example, the flash point will be as follows:

$$\text{Flash point} = 0.77(420 - 150) = 208\,^\circ\text{F}.$$

Blending Products of Different Flash Points

As with pour points and viscosity, the flash point of a blend of two or more components is determined by using a flash blending index. Figure 13 gives these indices. Again the indices are blended linearly as in the case of viscosity. Consider the following example:

2,000 BPSD of kerosene with a flash point of 120 °F is to be blended with 8,000 BPSD of fuel oil with a flash point of 250 °F. Calculate the flash point of the blend (Table 8).

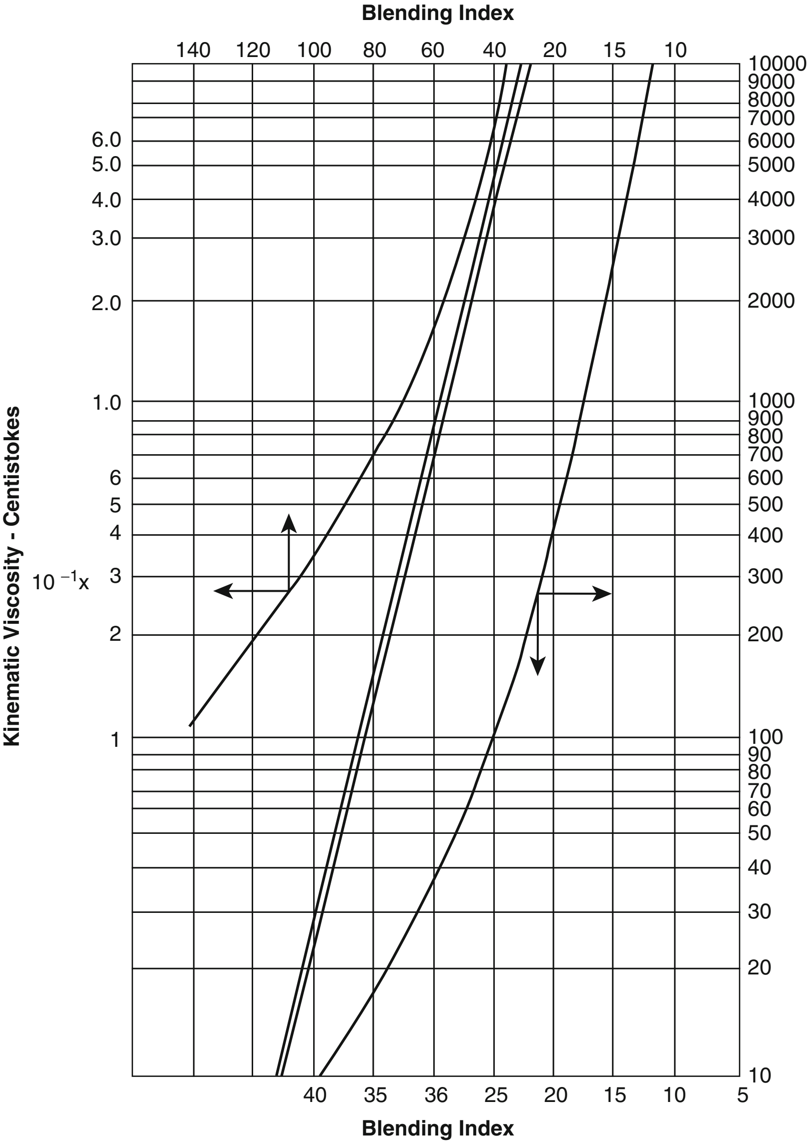


Fig. 11 Viscosity blending index

Predicting the Mole Weights of Products

The prediction of molecular weights of product streams is often required for the design of the processes that are going to produce those products. There are other more rigorous calculations that can and are used for definitive design and in

Table 6 Calculating the viscosity of a cut

Component	Volume %	Mid-BPt °F	Viscosity cS 100 °F	Blending index	Viscosity factor
	(A)			(B)	(A × B)
1	13.0	410	1.49	63.5	825.5
2	16.5	460	2.0	58.0	957
3	21.0	489	2.4	55.0	1,155
4	18.0	520	2.9	52.5	945
5	18.5	550	3.7	49.0	906.5
6	13.0	592	4.8	46.0	598
Total	100.0				5,387.0

Overall viscosity index $= \frac{5,387}{100} = 53.87$

From Fig. 11 an index of 53.87 = 2.65 cSt (actual plant test data was 2.7 cSt)

building up computer simulation packages. The method presented here is a simple method by which the mole weight of a product stream can be determined from a laboratory ASTM distillation test. The result is sufficiently accurate for use in refinery configuration studies and the like.

A relationship exists between the mean average boiling point of a product (commonly designated as MEABP), the API gravity, and the molecular weight of petroleum fractions. This is shown in Fig. 14.

Using a gas oil fraction as an example, the MEABP of the product is calculated from its ASTM distillation in degrees Fahrenheit as given below:

% Vol	°F
0	406
10	447
30	469
50	487
70	507
90	538
100	578

$$\text{The slope of the curve is calculated by } \frac{T{}^\circ\text{F}@\,90\% - T{}^\circ\text{F}@\,10\,\%}{80} = \frac{538 - 447}{80} = 1.14\ {}^\circ\text{F}\% \tag{5}$$

$$\text{Volume average boiling point} = \frac{T{}^\circ\text{F}@\ 10\,\% + (2 \times T{}^\circ\text{F}@\,50\ \%) + T\ {}^\circ\text{F}@\,90\%}{4} = \frac{447 + 974 + 538}{4} = 490{}^\circ\text{F} \tag{6}$$

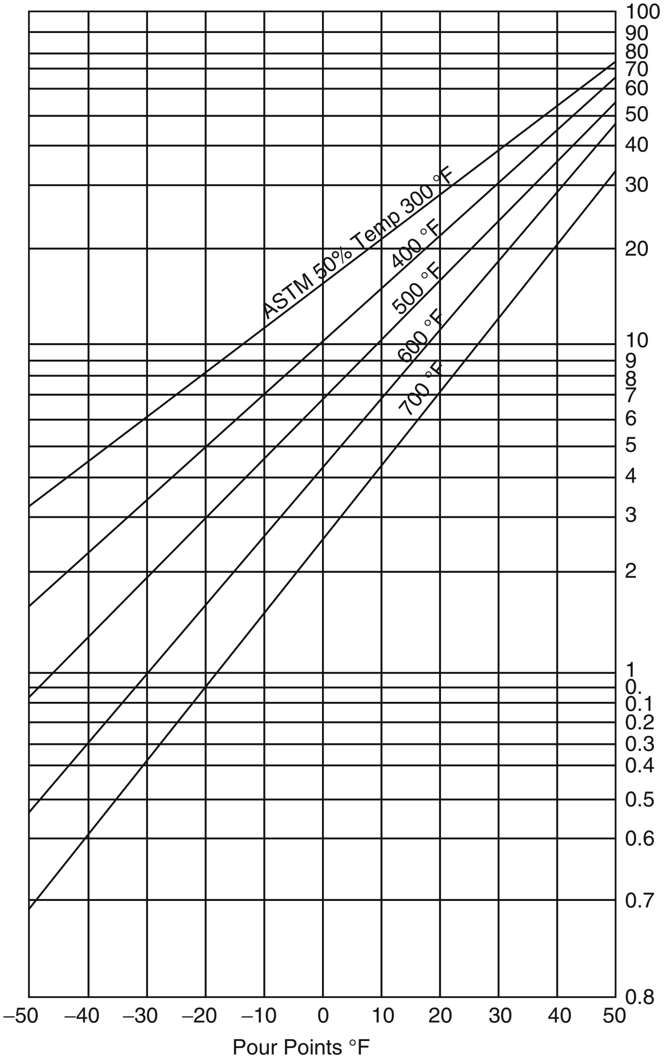


Fig. 12 Pour point blending index

Table 7 Calculating pour points of a cut

	Composition		ASTM dist		Pour point		
Components	BPSD	Fraction	50 % °F	Factor	Pour point °F	Index	Factor
Gas oil	2,000	0.33	500	85.8	−5	5.8	1.9
Waxy dist	4,000	0.67	700	249	30	12.7	8.5
Total	6,000	1.00	634	334	22		10.4

The pour point of the blend is read from Fig. 12 where the ASTM 50 % point is 634 °F and the index is 10.4. In this case the pour point is 22 °F

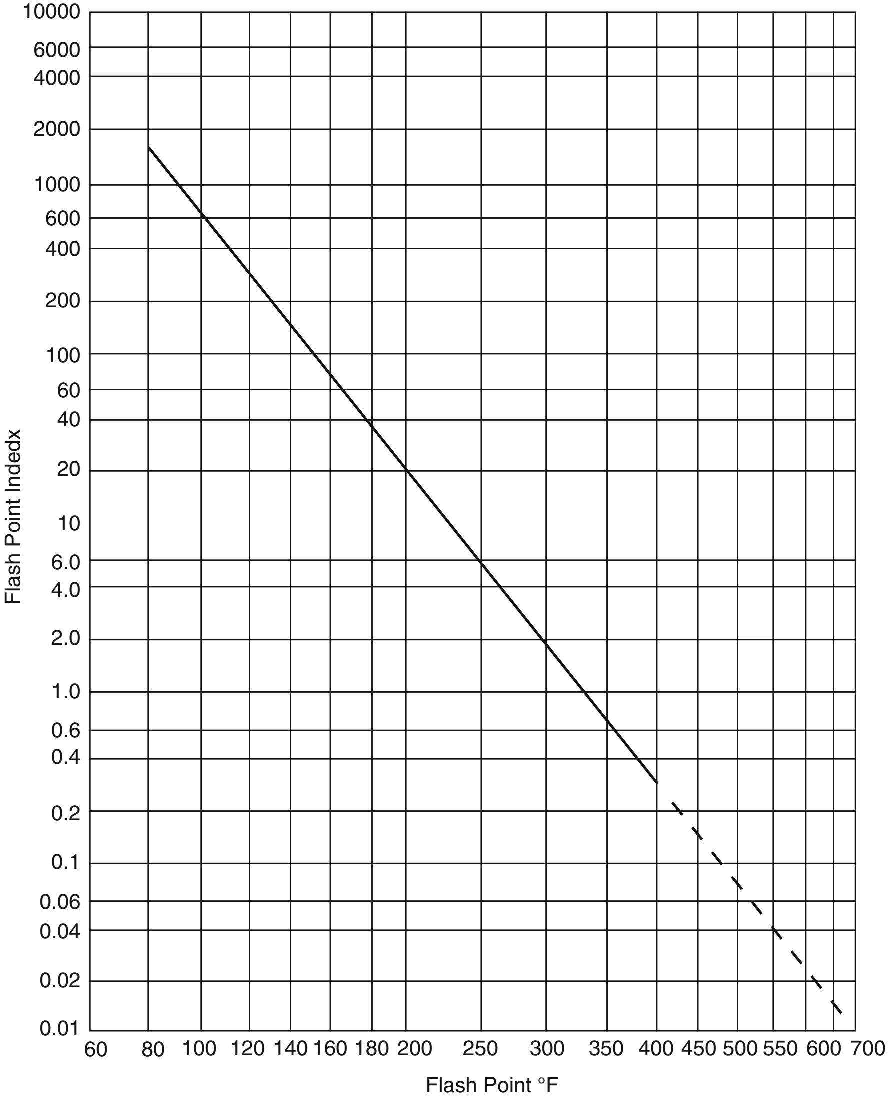


Fig. 13 Flash point blending index

Table 8 Blending streams for flash points

Components	Volume BPSD	Fraction (A)	Flash point, °F	Flash index (B)	Factor (A × B)
Kerosene	2,000	0.2	120	310	62.0
Fuel oil	8,000	0.8	250	5.5	4.4
Total	10,000	1.0			66.4

The flash point corresponding to an index of 66.4 (from Fig. 13) is 166 °F

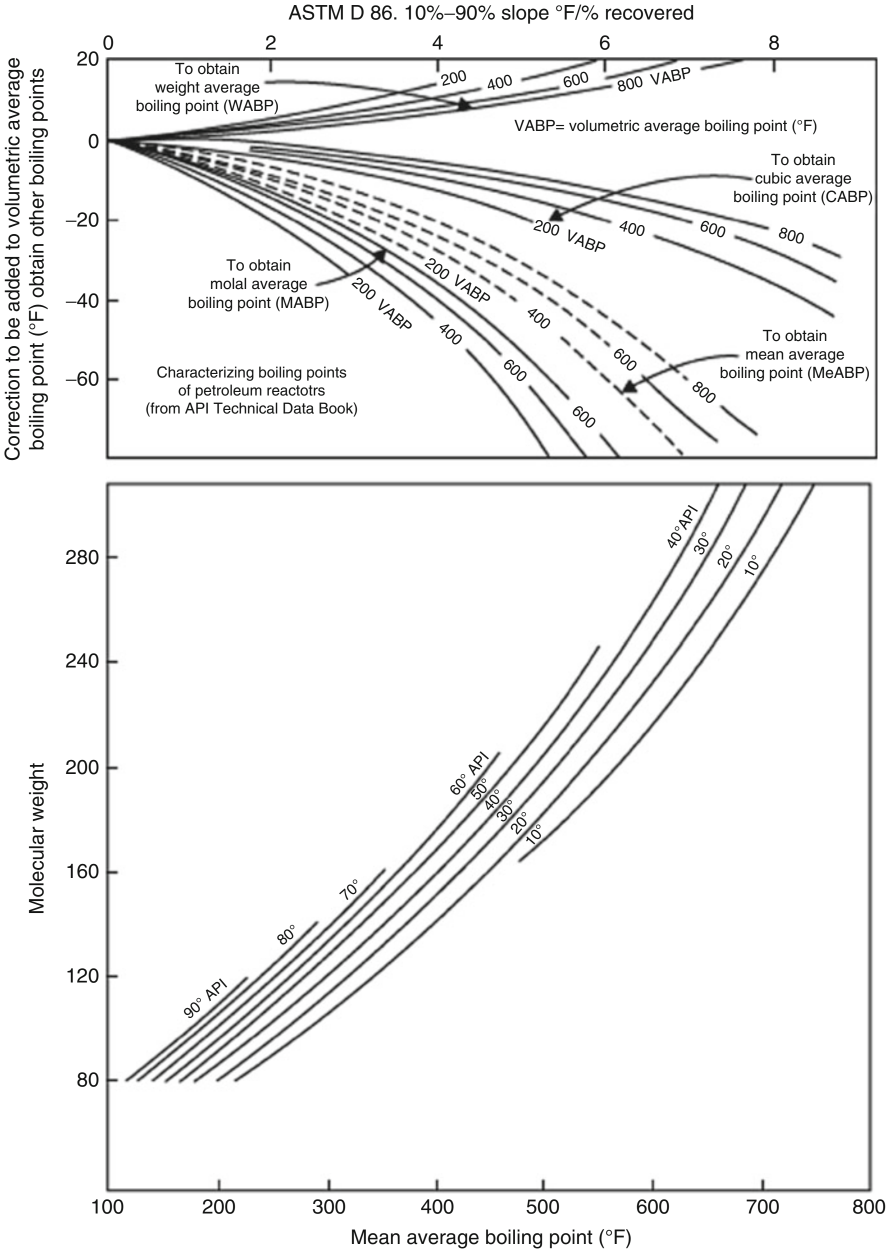


Fig. 14 Correlation between boiling point, molecular weight, and gravity

From the upper series of curves given in Fig. 14, the correction to the volumetric average boiling point (VABP) to obtain the mean average (MEABP) is −5 °F. Thus, the MEABP is

$$490 + (-5) = 485\ ^\circ\mathrm{F}$$

The °API of the stream from the calculation for gravity is 38.8. Using this figure and the MEABP in the lower series of curves in Fig. 14, a molecular weight of 201 is read off.

Basic Petroleum Refining Processes

This chapter provides an introduction to some of the most common processes included in fuel-oriented and nonenergy-oriented refineries. These processes are only discussed here in summary form. They are treated in more detail later in individual topics and chapters.

The Atmospheric Crude Distillation Unit

In refining the crude oil, it is first broken up into those raw stocks that are the basis of the finished products. This breakup of the crude is achieved by separating the oil into a series of boiling point fractions which meet the distillation requirements and some of the properties of the finished products. This is accomplished in the crude distillation units. Normally there are two units that accomplish this splitting up function: an atmospheric unit and a vacuum unit.

The crude oil is first desalted (dissolved brine is removed by washing) and heated to a predetermined temperature prior to its introduction into the atmospheric unit. This is accomplished by heat exchange with hot products and finally by a direct fired heater. The hot and partially vaporized crude is "flashed" in a trayed distillation tower. Here, the vaporized portion of the crude oil feed moves up the tower and is selectively condensed by cooled reflux streams moving down the tower. These condensates are taken off at various parts of the tower according to their condensing temperature as distillate side streams. The light oils not condensed in the tower are taken off at the top of the tower to be condensed externally as the overhead product. The unvaporized portion of the crude oil feed leaves the bottom of the tower as the atmospheric residue.

The unit operates at a small positive pressure around 5–10 psig in the overhead drum, thus its title of "atmospheric" crude unit. Typical product streams leaving the distillation tower are as follows:

Overhead distillate	Full-range naphtha	Gas to 380 °F cut point
1st side stream	Kerosene	380–480 °F cut range
2nd side stream	Light gas oil	480–610 °F cut range
3rd side stream	Heavy gas oil	610–690 °F cut range
Residue	Fuel oil	+690 °F cut point

Full details of this unit are given in the chapter entitled "▶ Atmospheric and Vacuum Crude Distillation Units in Petroleum Refineries."

The Crude Vacuum Distillation Unit

Further breakup of the crude is often required to meet the refinery's product slate. This is usually required to produce low-cost feed to cracking units or to produce the basic stocks for lubricating oil production. To achieve this, the residue from the atmospheric unit is distilled under subatmospheric conditions in the crude vacuum distillation unit. This unit is similar to the atmospheric unit in so much as the feed is heated by heat exchange with hot products and then in a fired heater before entering the distillation tower. In this case, however, the tower operates under reduced pressure (vacuum) conditions. These units operate at overhead pressures as low as 10 mmHg. Under these conditions the hot residue feed is partially vaporized on entering the tower. The hot vapors rise up the tower to be successively condensed by a cooled internal reflux stream moving down the tower as was the case in the atmospheric distillation unit. The condensed distillate streams are taken off as side stream distillates. There is normally no overhead distillate stream in this case.

The high vacuum required in these units is produced by a series of steam ejectors attached to the unit's overhead system. Typical product streams from this unit are as follows:

Top side stream	Light vacuum gas oil	690–750 °F
2nd side stream	Heavy vacuum gas oil	750–985 °F
Residue	Bitumen	+985 °F

This unit is further described and discussed in the chapter entitled "▶ Atmospheric and Vacuum Crude Distillation Units in Petroleum Refineries."

The Light Ends Units

The full-range naphtha distillate as the overhead product from the atmospheric crude unit is further split into the basic components of the refinery's volatile and light oil products. This is accomplished in the light ends plant, which usually contains four separate distillation units. These are:

- The de-butanizer (or debutanizer)
- The de-propanizer (or depropanizer)
- The de-ethanizer (or deethanizer)
- The naphtha splitter

The most common routing of the full-range naphtha from the atmospheric crude overhead is first to the debutanizer unit. This feed stream is heated by heat exchange with hot products before entering the feed tray of the debutanizer column. This is a distillation column containing between 30 and 40 trays. Separation of butanes and lighter gas from the naphtha occurs in this tower by fractionation. The butanes and lighter are taken off as an overhead distillate, while the naphtha is removed as the column's bottom product. The overhead distillate is then heated again by heat exchange with hot streams and fed into a depropanizer column. This column also has about 30–40 distillation trays and separates a butane stream from the propane and lighter material stream by fractionation. The butanes leave as the column's bottom product to become the butane LPG product after further "sweetening" treatment (sulfur removal). The column's overhead distillate is fed to a deethanizer column after preheating. Here the propane is separated from the lighter materials and leaves the column as the bottom product. This stream becomes part of the refinery's propane LPG product after some further "sweetening" treatment. There will be no overhead distillate product from this unit. The material lighter than propane leaves the overhead drum as a vapor containing mostly ethane and is normally routed to the refinery's fuel gas system.

The debutanized naphtha leaving the bottom of the debutanizer is subsequently fractionated in the naphtha splitter to give a light naphtha stream as the overhead distillate and a heavy naphtha as the column's bottom product. The light naphtha is essentially C5s and nC6s; this stream is normally sent to the refinery's gasoline pool as blending stock. The heavy naphtha stream contains the cycloparaffin components and the higher paraffin isomers necessary to make good catalytic reformer feed. This stream therefore is sent to the catalytic reformer after it has been hydrotreated for sulfur and nitrogen removal.

The light end units are further described and discussed in the chapter entitled "▶ Distillation of the "Light Ends" from Crude Oil in Petroleum Processing."

The Catalytic Reformer Unit

The purpose of the catalytic reformer plant is to upgrade low-octane naphtha to the high-octane material suitable for blending into motor gasoline fuel. It achieves this by reforming some of the hydrocarbons in the feed to hydrocarbons of high-octane value. Notably among those reactions is the conversion of cycloparaffin content of the feed to aromatics. This reaction also gives up hydrogen molecules which are subsequently used in the refinery's hydrotreating processes.

The feed from the bottom of the naphtha splitter is hydrotreated in the naphtha hydrotreater for the removal of sulfur and nitrogen. It leaves this unit to be preheated to the reforming reaction temperature by heat exchange with products and by a fired heater. The feed is mixed with a recycle hydrogen stream before entering the first of (usually) three or four reactors. The reforming reactions take place in these reactors and the reactor temperatures are sustained and controlled by intermediate fired heaters. The effluent leaves the last reactor to be cooled and partially condensed by heat exchange with cold feed and a condenser. This cooled effluent is routed to a flash drum from which a hydrogen-rich stream is removed as a gas while reformate is removed as a liquid stream and sent to a stabilizer column. The bottom from this column is debutanized reformate and is routed to the gasoline pool for blending to meet motor gasoline specifications. Part of the gas leaving the flash drum is recycled to the reactors as the unit's recycle stream. The remaining gas is normally sent to the naphtha hydrotreater for use in that process. There is also a continuous version of this process available.

Details of the catalytic reforming process are described and discussed further in the chapter entitled "▶ Catalytic Reforming in Petroleum Processing."

The Hydrotreating Units (de-sulfurization)

Most streams from the crude distillation units contain sulfur and other impurities such as nitrogen and metals in some form or other. By far the most common of these impurities is sulfur, and this is also the least tolerable of these impurities. Its presence certainly lowers the quality of the finished products and, in the processing of the crude oil, its presence invariably affects the performance of the refining processes. Hydrotreating the raw distillate streams removes a significant amount of the sulfur impurity by reacting the sulfur molecules with hydrogen to form hydrogen sulfide (H_2S); this is then removed as a gas.

Several types of hydrotreaters are described in this book. The two most common types found are:

- Naphtha hydrotreating – once through or recycle hydrogen
- Diesel hydrotreating – recycle hydrogen

In naphtha hydrotreating the naphtha from the naphtha splitter is mixed with the hydrogen-rich gas from the catalytic reformer unit and preheated to about 700 °F by heat exchange and a fired heater. On leaving the fired heater, the stream enters a reactor containing a desulfurizing catalyst (often Co Mo – cobalt molybdenum – on an alumina base). The sulfur components of the feed combine with the hydrogen to form H_2S. The effluent from the reactors is cooled and partially condensed before being flashed in a separator drum. The gas phase from this drum is still high in hydrogen content and is usually routed to other downstream hydrogen-using processes. This stream contains most of the H_2S produced in the reactors; the remainder leaves the flash drum with the desulfurized naphtha liquid to be removed in the hydrotreater's stabilizer column as an H_2S-rich gas.

Diesel hydrotreating has very much the same process configuration as the naphtha unit. The main difference is that this unit will almost invariably have a rich hydrogen stream recycle. The recycle is provided by the flashed gas stream from the flash drum. This is returned to mix with the feed and a fresh hydrogen make up stream before entering the preheater system. The recycle gas stream in these units is often treated for the removal of H_2S before returning to the reactors.

A detailed discussion and description of these processes are given in the chapter entitled "▶ Hydrotreating in Petroleum Processing."

The Fluid Catalytic Cracking Unit (FCCU)

This cracking process is among the oldest in the oil industry. Although developed in the mid-1920s, it first came into prominence during the Second World War as a source of high-octane fuel for aircraft. In the early 1950s its prominence as the major source of octane was somewhat overshadowed by the development of the catalytic reforming process with its production of hydrogen as well as high-octane material. The prominence of the fluid catalytic cracking unit (FCCU) was reestablished in the 1960s by two developments in the process. These were:

- The use of highly active and selective catalysts (Zeolites)
- The establishment of riser cracking techniques

These two developments enabled the process to produce higher yields of better-quality distillates from lower-quality feedstocks. At the same time catalyst inventory and consumption costs were significantly reduced.

The process consists of a reactor vessel and a regenerator vessel interconnected by transfer lines to enable the flow of finely divided catalyst powder between them. The oil feed (typically high-vacuum gas oil, HVGO, from the crude vacuum unit) is introduced to the very hot regenerated catalyst stream leaving the regenerator en route to the reactor. Cracking occurs in the riser inlet to the reactor due to the contact of the oil with the hot catalyst. The catalyst and oil are very dispersed in the riser so that contact between them is very high exposing a large portion of the oil to the hot catalyst. The cracking is completed in the catalyst fluid bed in the reactor vessel. The catalyst fluidity is maintained by steam injection at the bottom of the vessel. The cracked effluent leaves the top of the reactor vessel as a vapor to enter the recovery section of the plant. Here the distillate products of cracking are separated by fractionation and forwarded to storage or further treating. An oil slurry stream from this recovery plant is returned to the reactor as recycle.

The catalyst from the reactor is transferred to the regenerator on a continuous basis. In the regenerator the catalyst is contacted with an air stream which maintains the catalyst in a fluidized state. The hot carbon on the catalyst is burned off by contact with the air and converted into CO and CO_2. The reactions are highly exothermic rising the temperature of the catalyst stream to well over 1,000 °F and thus providing the heat source for the oil cracking mechanism.

Products from this process are:

- Unsaturated and saturated LPG
- Light cracked naphtha
- Heavy cracked naphtha
- Cycle oil (mid distillate)
- Slurry

Details of this process together with typical yield data are given in the chapters on "▶ Fluid Catalytic Cracking (FCC) in Petroleum Refining" and "▶ Upgrading the Bottom of the Barrel."

The Hydrocracking Process

This process is fairly new to the industry becoming prominent in its use during the late 1960s. As the title suggests the process cracks the oil feed in the presence of hydrogen. It is a high-pressure process operating normally around 2,000 psig. This makes the unit rather costly and, for many years, slowed its expansion in the industry compared with the FCCU and thermal cracking. However, the process is very flexible and is capable of making modern, high- quality distillate fuels and lubes. It can handle a wide spectrum of feeds including straight run gas oils, vacuum gas oils, thermal cracker gas oils, FCCU cycle oils, and the like. The products it produces need very little downstream treating to meet finished product specifications. The naphtha stream it produces is particularly high in naphthenes making it a good catalytic reformer stock for gasoline or aromatic production.

The process consists of one or two reactors, a preheat system, recycle gas section, and a recovery section. The oil feed (typically a vacuum gas oil) is preheated by heat exchange with reactor effluent streams and by a fired heater. Make-up and recycled hydrogen streams are introduced into the oil stream before entering the reactor(s). (Note: in some configurations the gas streams are also preheated prior to joining the oil.) The first section of the reactor is often packed with a hydrotreating catalyst to protect the more sensitive cracking catalyst further down in the reactor from injurious sulfur, nitrogen, and metal poisoning. Cracking occurs in the reactor(s) and the effluent leaves the reactor to be cooled and partially condensed by heat exchange. The stream enters the first of two flash drums. Here, the drum pressure is almost that of the reactor. A gas stream rich in hydrogen is flashed off and is recycled back to the reactors as recycle gas. The liquid phase from the flash drum is routed to a second separator which is maintained at a much lower pressure (around 150–100 psig). Because of this reduction in pressure, a second gas stream is flashed off. This will have a much lower hydrogen content but will contain C_3s and C_4s. For this reason the stream is often routed to an absorber column for maximizing LPG recovery. The liquid phase leaves the bottom of the low-pressure absorber to enter the recovery side where products are separated by fractionation and sent to storage.

Further details of this process are given in the chapters entitled "▶ Hydrocracking in Petroleum Processing", "▶ Upgrading the Bottom of the Barrel, and "▶ Non-energy Refineries in Petroleum Processing".

Thermal Cracking Units

Thermal cracking processes are the heavy work horses of the oil refining industry. The processes are relatively cheap when compared with the fluid cracker and the hydrocracker but go a long way to achieving the heavy oil cracking objective of converting low-quality material into more valuable oil products. The process family of thermal crackers has three members, which are:

- Thermal crackers
- Visbreakers
- Cokers

The term thermal cracking is given to those processes that convert heavy oil (usually fuel oil or residues) into lighter product stock such as LPG, naphtha, and middle distillates by applying only heat to the feed over a prescribed element of time. The term thermal cracker when applied to a specific process usually refers to the processing of atmospheric residues (long residues) to give the lighter products. The term visbreaking refers to the processing of vacuum residues (short residues) to reduce the viscosity of the oil only and thus to meet the requirements of a more valuable fuel oil stock. Coking refers to the most severe process in the thermal cracking family. Either long or short residues can be fed to this process whose objective is to produce the lighter products and petroleum coke. The coker process is extinctive – that is, it converts all the feed. In the other two processes, there is usually some unconverted feed although the thermal cracker can be designed to be “extinctive” by recycling the unconverted oil. The three thermal cracking processes have the same basic process configuration. This consists of a cracking furnace, a “soaking” vessel or coil, and a product recovery fractionator(s). The feed is first preheated by heat exchange with hot product streams before entering the cracking furnace or heater. The cracking furnace raises the temperature of the oil to its predetermined cracking temperature. This is always in excess of 920 °F and, by careful design of the heater coils, the oil is retained in the furnace at a prescribed cracking temperature for a predetermined period of time (the residence time). In some cases an additional coil section is added to the heater to allow the oil to “soak” at the fixed temperature for a longer period of time. In other cases the oil leaves the furnace to enter a drum which retains the oil at its cracking temperature for a little time. In the coker process, the oil leaves the furnace to enter one of a series of coker drums in which the oil is retained for a longer period of time at its coking temperature for the production of coke.

The cracked oil is quenched by a cold heavy oil product stream on leaving the soaking section to a temperature below its cracking temperature. It then enters a fractionator where the distillate products are separated and taken off in a manner similar to the crude distillation unit. In the case of the cokers, the coke is removed from the drums by high-velocity water jets on a regular batch basis. The coking process summarized here refers to the more simple “delayed coking” process. There are other coking processes which are more complicated such as the fluid coker and the proprietary Flexicoker.

Further details on thermal cracking are provided in the chapter “▶ Upgrading the Bottom of the Barrel.” This chapter includes also the treating of residues by hydrocracking and fluid catalytic cracking.

Gas Treating Processes

The processes summarized above are the more common ones to be included in a fuel or energy refinery's configuration. In addition to these, there will also be the gas treating processes and often sulfur recovery processes. These are described and discussed in the chapters "▶ Refinery Gas Treating Processes" and "▶ Environmental Control and Engineering in Petroleum Processing."

Gas treating is always required to remove the H_2S impurity generated by hydrotreating or cracking from the refinery fuel gas or hydrogen recycle streams. The removal of H_2S for these purposes is accomplished by absorbing the hydrogen sulfide into an amine or similar solution that readily absorbs H_2S. Stripping the rich absorbent solution removes the H_2S from the system to be further reacted with air to produce elemental sulfur. This latter reaction takes place in a specially designed sulfur plant.

The rich H_2S-laden gases from all the refinery sources enter below the bottom tray (or packed bed) of the absorber tower. The lean, low-H_2S absorbent solution enters the tower above the top tray (or packed bed) to move down the tower countercurrent to the gas moving upward. Mixing on the trays (or packed beds) allows the H_2S from the gas phase to be absorbed into the liquid solution phase. The H_2S-free gas ($< \sim 100$ vppm H_2S) leaves the tower top to be routed to refinery fuel or other prescribed destination.

The rich absorbent solution leaves the bottom of the absorber to be heat exchanged with hot stripped absorbent solution before entering the feed tray of the stripping column. The solution moving down the tower is stripped of most H_2S by a stripper vapor phase moving up the tower. This stripper phase is generated by conventional reboiling of the bottom tray solution. The hot stripped solution leaves the bottom of the tower to be cooled by heat exchange with the feed and then by an air or water cooler before entering the absorber tower. Conditions in the stripper column are maintained by partially condensing the rich H_2S overhead vapors and then returning the distillate as reflux to the top tray of the rectifying section of the tower (which is the section of trays above the feed tray).

The vapor not condensed leaves the reflux drum to be routed to a sulfur plant. These vapors contain a high concentration of H_2S (usually in excess of 90 % mol) and enter the specially designed fuel "gun" of the sulfur plant heater. Here, about one third is mixed with an appropriate concentration of air and "burned" in the plant's fire box to generate SO_2. The gases generated are combined with the remaining H_2S and passed over a catalyst bed where almost complete conversion to elemental sulfur occurs. This product, in molten form, enters a heated storage pit or tank. The unconverted sulfurous vapors are further incinerated before venting to atmosphere from an acceptably elevated location. Sulfur recovery is detailed in the chapter on "▶ Environmental Control and Engineering in Petroleum Processing."

Processes Not So Common to Energy Refineries

Octane Enhancement Processes

The octane enhancement processes detailed in this book are the alkylation process and the isomerization process. These processes are usually proprietary and are provided to refiners under license.

The alkylation process treated here is the HF process which uses hydrogen fluoride as the catalyst which is used to convert unsaturated C_4s and iC_4 to high-octane alkylate. The unit's recovery side is the aspect dealt with in some detail together with a descriptive item on the safe handling of hydrogen fluoride. An alternative alkylation process uses sulfuric acid, H_2SO_4, instead of HF.

The isomerization process has a similar configuration to the catalytic reformer plant. This process uses hydrogen in its conversion of low-octane hydrocarbons to higher-octane isomers.

Both these processes are described and discussed in detail in the chapters on "▶ Alkylation in Petroleum Processing" and "▶ Isomerization in Petroleum Processing."

Oxygenated Gasolines

The concentration of vehicles on the roads in most of the cities in the modern world has increased dramatically over the last two decades. The emission of pollutants from these vehicles is causing a significant addition to the already critical problem of atmospheric pollution. The problem is now so acute that governments of most developed countries are seeking legislation to curb and minimize this pollution and most countries will see further implementation of "Clean Air" acts.

Petroleum refining companies have been working diligently for many years to satisfy the requirements of "Clean Air" legislation already in place. This began in the 1970s with the elimination of tetraethyl lead from most gasoline applications. Processes such as isomerization and polymerization of refinery streams were developed together with a surge in the use of the alkylation process. However, the further decrease of pollutants now requires a move away from the traditional gasoline octane enhancers such as the aromatics and the olefins.

Catalytic reforming produces gasoline streams to meet octane requirements mainly by converting cycloparaffin to light aromatics. Fluid catalytic cracking also produces gasoline blending stocks by cracking paraffins to light olefins and the products from these two processes still make up the bulk of a refinery's gasoline pool. Unfortunately the aromatics are "dirty compounds" because they produce a sooty exhaust emission – unacceptable in meeting the "Clean Air" requirements and the aromatics are considered "toxics". Considerable work has been done with alcohol to take the place of aromatics and as octane enhancers and meeting other gasoline specs such as RVP. Essentially all companies in North America use ethanol in the gasoline blend by Federal mandate.

Much success in reducing aromatics in gasoline to date however has been in the production and blending of oxygenated compounds into the gasoline pool, but mostly outside the USA. A press release by a number of companies in 1990 is quoted as follows:

- Adding oxygenates reduces the amount of exhaust emissions (hydrocarbons and carbon monoxide) and the benefits have been quantified.
- Changing the level of olefins in gasoline does not have much of an impact on vehicle exhaust emission.
- Reducing aromatics and/or boiling range of gasoline can either reduce or increase exhaust emissions depending upon vehicle type.

Oxygenates are ether compounds derived from their respective alcohol. There are three candidates of these ethers to meet the gasoline requirements. These are:

- Methyl tertiary butyl ether (MTBE)
- Ethyl tertiary butyl ether (ETBE)
- Tertiary amyl methyl ether (TAME)

Of these three candidates MTBE is the one that has been used more extensively to meet all the gasoline pool objectives. This compound has the blending quality of 109 octane, an RVP blending of 8–10 psi, and a boiling point of 131 °F.

ETBE octane blending properties seem to be slightly better than those of MTBE and so does its RVP blending qualities. The ethanol feed stream of course is not as readily available as methanol and requires a separate production unit, often by means of fermentation of organic materials.

TAME has an average octane number of 104 and an RVP blending of 3–5 psi. Except for the lower octane value, TAME has similar blending properties to ETBE. The ether in this case is formed by the reaction of 2-methyl-2-butene and 2-methyl-1-butene olefin feed and methanol. Commercial plants operate in the UK and parts of Europe producing TAME. The compound is used in Europe as a gasoline product and not as a gasoline blend stock. The front end of a cracked gasoline stream is used in this manufacture to provide the olefin.

Use of MTBE has been phased out in the USA because of groundwater contamination (MTBE has a very unpleasant smell) but is still in use in Europe and elsewhere. However, emphasis on the use of renewable resources in Europe has prompted a gradual shift from MTBE to ETBE.

The Production of Ethers for Gasoline Blending

There are several licensed processes for the production of methyl tertiary butyl ether by the etherification of a C_4/C_5 olefin stream and methanol. These processes

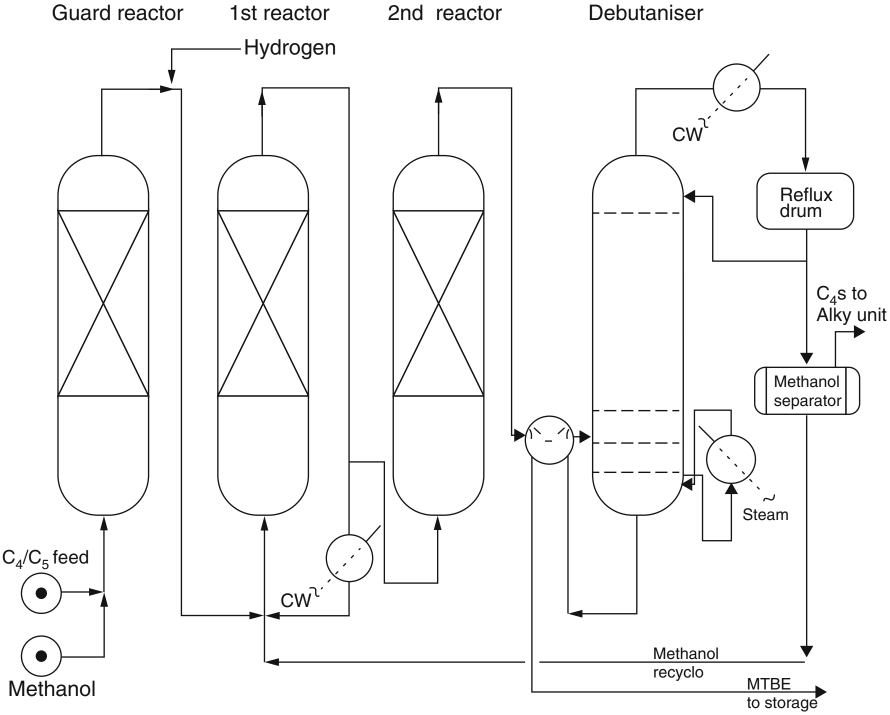


Fig. 15 Typical flow diagram for the production of MTBE

have very similar configurations and are flexible enough to be converted quite simply to the production of the other ethers. Figure 15 is a typical flow diagram for this process.

The olefin feed from a FCCU or a steam cracker is combined with a methanol stream to enter a guard reactor to remove impurities. A small hydrogen stream is added to the hydrocarbon from the guard reactor prior to entering the ether reactor. This reactor contains a special acid resin catalyst (usually a cross-linked sulfonic resin) and the reactor feed flows upward through this catalyst bed at moderate temperature and pressure and in the liquid phase. The reaction is exothermic and temperature control is maintained by externally cooling a recycle stream from the first of two reactor vessels.

The catalyst in this case performs three reactions simultaneously: etherification of branched olefins, selective hydrogenation of the unwanted diolefins, and hydroisomerization of olefin by a double-bond switch. The reactor effluent leaves the top of the second reactor vessel to be heated in a feed heat exchanger with the debutanizer bottoms product. The overheads from the debutanizer are a C_4 and methanol stream. The methanol stream is recycled to the first reactor, while the C_4s are returned to the FCCU light end unit. The bottom product is C_5+ enriched with MTBE (or TAME depending on the olefin feed used).

The production of oxygenated gasolines is described and discussed further in the chapter on “▶ Petroleum Products and a Refinery Configuration.”

The Nonenergy Refineries

In addition to the energy-related refineries, which occupy most of this book, there are two major types of nonenergy-producing refineries. These are the lube oil refinery and the petrochemical refineries. These are summarized below:

The Lube Oil Refinery

The schematic flow diagram (Fig. 16) shows a typical lube oil-producing refinery configuration. In this case, the processes used involve extraction and dewaxing of conventional petroleum stocks. Only about eight or nine base lube oil stocks are produced from refinery streams. The many hundreds of commercial grades of lubricating oils used in industry and transportation are blends of these base stocks with some small amounts of proprietary additives (mostly organic acid derivatives) included to meet their required specifications. There are also two quite important by-products of lube oil. These are bitumen and waxes. Most refineries include bitumen blending in their configuration, but only a few of the older refineries process the waxes. These are exported to manufacturers specializing in wax and grease production.

Newer lube oil production processes are based on:

- High-temperature and high-pressure hydrocracking, hydrodewaxing, and hydrofinishing
- Conversion of natural gas to liquids (GTL) with subsequent hydrocracking and hydrodewaxing/finishing

While the extraction/dewaxing approach is still used for some oils, most new engine oils require the product qualities produced by the hydrocracking or GTL processes. It is still instructional to understand the needs for lube oils by reviewing the older process scheme.

Lube oil production starts with the vacuum distillation of atmospheric residue. This feedstock is usually cut into three distillate streams each meeting a boiling range which gives streams with viscosity meeting the finished blending product specifications. The lighter stream is taken off as the top side stream and is further distilled again under vacuum to three light lube oil blending cuts. These are called spindle oils and, when finished, will form the basis of light lubes used for domestic purposes such as sewing machine, bicycle, and other home lubricant requirements. Some of the heavier spindle oils are also used as blend stocks for light motor oils. These spindle oils require very little treatment for finishing. Usually, a mild hydrotreating suffices to meet the color requirement.

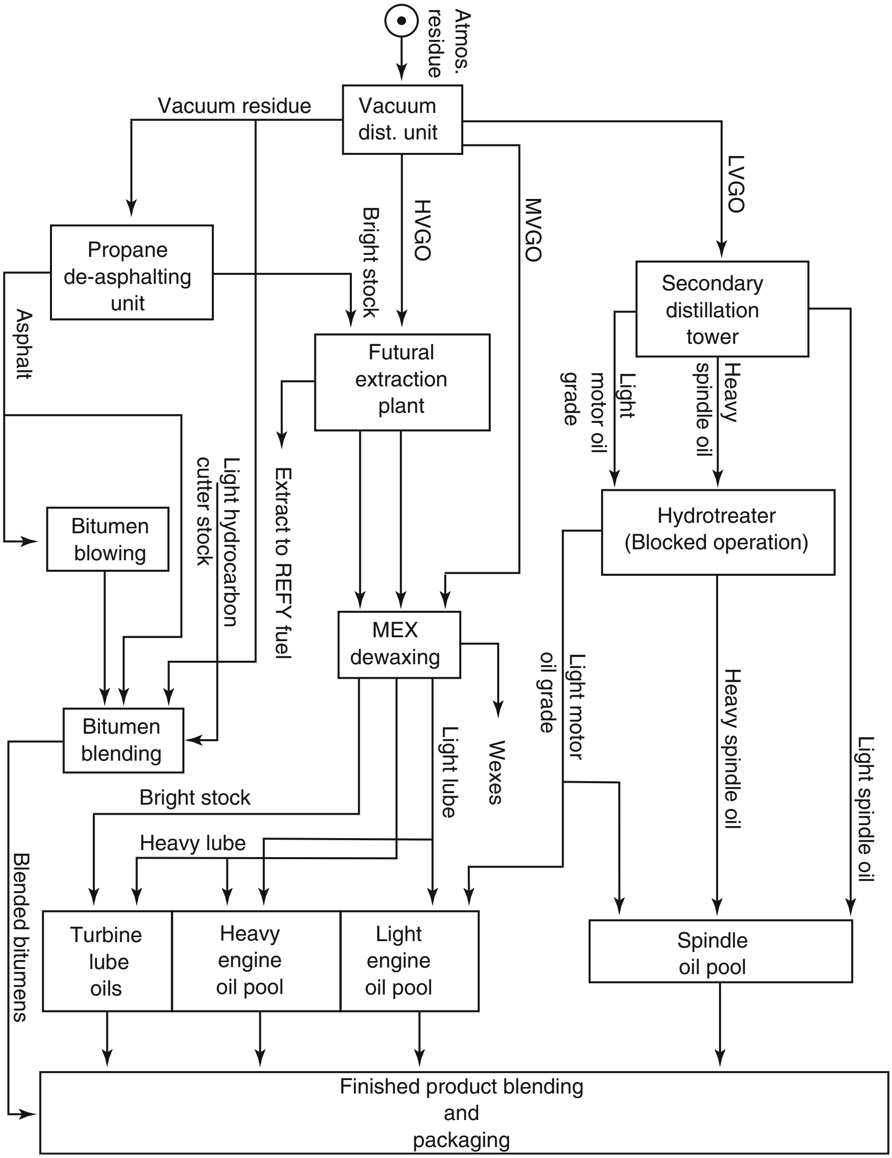


Fig. 16 A lube oil refinery configuration

The second distillate side stream is dewaxed and sent to the engine lube oil pool. It may also be blended with the heavier bottom side stream as heavy engine oil stock. The bottom side stream is one of the base blending stocks for heavy engine oils and the turbine oil stocks. To meet color and other specifications, these heavier oils must be treated for the removal of undesirable components (such as heavy aromatics and olefins) by solvent extraction. This is accomplished prior to the stream being dewaxed and routed to storage. The heavy vacuum residue from the vacuum tower is routed to a propane deasphalting unit. Here, the very thick bituminous asphaltenes are removed by extraction with liquid propane. The raffinate from this extraction process is the heaviest lube oil blending stream commonly called bright stock. This stream is also routed to the solvent extraction unit and the dewaxing process before storage.

Solvent extraction is accomplished in a trayed column by contacting the oil feed and solvent countercurrently in the tower. The lighter raffinate stream leaves the top of the tower to be stripped free of the solvent in an associated stripper column, before entering the dewaxing unit. The extracted components leave the bottom of the tower also to be stripped free of the solvent in an associated stripper column. The extract in this case may be routed to the propane deasphalting unit or simply sent to the refinery fuel supply. The solvent in modern refineries is either furfural, phenol, or a proprietary solvent based on either of these chemicals. In earlier plants oleum or liquid SO_2 was used for this purpose.

The oil streams routed to the dewaxing plant are contacted and mixed with a crystallizing agent such as methyl-ethyl-ketone (MEK) before entering a series of chiller tubes. Here the oil/MEK mix is reduced in temperature to a degree that the wax contained in the oil crystallizes out. The stream with the wax now in suspension enters a series of drum filters where the wax and oil are separated. Both streams are stripped free of the MEK in separate columns. The MEK is recycled while the dewaxed oil is sent to storage and blending. The wax may be retained as a solid in a suitably furnished warehouse or remelted and stored in special tanks with inert gas cover.

The asphalt from the propane deasphalting unit is stripped free of propane and any other light ends using inert gas as the stripping agent. It leaves the unit to proceed either directly to the bitumen pool or to be further treated by air blowing. The air-blowing process increases the hardness of the bitumen where this is required to meet certain specifications. It is accomplished either as a batch process or on a continuous basis. The hot stripped asphalt from the deasphalting unit enters the air blower reactor under level control (if the process is continuous). Air is introduced via a small compressor to the bottom of the reactor vessel and allowed to bubble up through the hot oil phase. The air removes some of the heavy entrained oils in the asphalt and reacts mildly to partially oxidize the asphaltenes. The hot oil vapors and the unused air leaves the top of the reactor to be burned in a suitably designed incinerator. The blown asphalt leaves the reactor as a side stream to bitumen storage or blending.

The production of lube oils usually takes place in a section of an energy refinery. The various grades of the oils are also produced in a blocked operation using storage facilities between the units. This is feasible as the amount of lube oils required to be produced is relatively small and normally does not justify separate treating facilities for each grade.

The lube oil refinery is further detailed in the chapter "▶ Non-energy Refineries in Petroleum Processing."

The Petrochemical Refinery

Feedstocks for the production of petrochemicals originate from refineries with processes similar to those described earlier to produce fuels. Indeed, there are only a few refineries worldwide that cater only to petrochemical requirements. Most petrochemical feedstocks are produced by changing operating parameters of the normal fuel refinery processes. In catering for the petrochemical needs, much of the refinery product streams are tailored as follows:

- *Aromatic streams* – high in benzene, toluene, and xylenes
- *Olefin streams* – high in ethylene, propylene, and C_4s

Producing the Aromatic Feedstock

The production of aromatic feedstocks originates with the catalytic reforming of a refinery stream of a heavy naphtha range (say 120–420 °F) and rich in naphthenes. A typical stream that meets these criteria would be a naphtha stream from a hydrocracker. Thus, in order to meet petrochemical needs, a hydrocracker may form part of a fuel refinery configuration. This unit would be operated to maximize naphtha production. This would mean running the unit at a low space velocity with a higher oil recycle rate (i.e., most recovered product heavier than the naphtha would be recycled back to the reactors).

Another source of high naphthene feed to the cat reformer would be hydrotreated cat cracker naphtha. Of course the hydrotreating of unsaturates has a high demand on the refinery’s hydrogen system, but this is balanced to some extent by the additional hydrogen produced in reforming the naphthenes. Should the refinery configuration include a thermal cracker and/or a steam cracker, the hydrotreating of the naphtha cut from these units also yields high naphthene catalytic reformer feedstock.

Catalytic reforming of the high naphthene-content naphtha produces aromatics, but there are also some unreacted paraffins and some naphthenes present. The downstream petrochemical units that separate and purify the aromatic reformate are expensive both in capital and operating costs. The specification for the BTX (benzene, toluene, xylene) feed is very stringent and excludes nonaromatic components as much as possible. Another process may therefore be included in the refinery configuration to “clean up” this aromatic feed stream before leaving the refinery. This is an aromatic extraction plant. This is a licensed process using a solvent to separate the paraffins and aromatics by countercurrent extraction. The rich aromatic stream is then forwarded to the BTX plant where benzene, toluene, ethyl benzene, and o-xylene are separated by fractionation while the para-xylene is usually separated by crystallization or by solid adsorption. The meta-xylene may also be recovered by super distillation, but more often than not, it is converted into *o*-xylene or *p*-xylene in an isomerization unit.

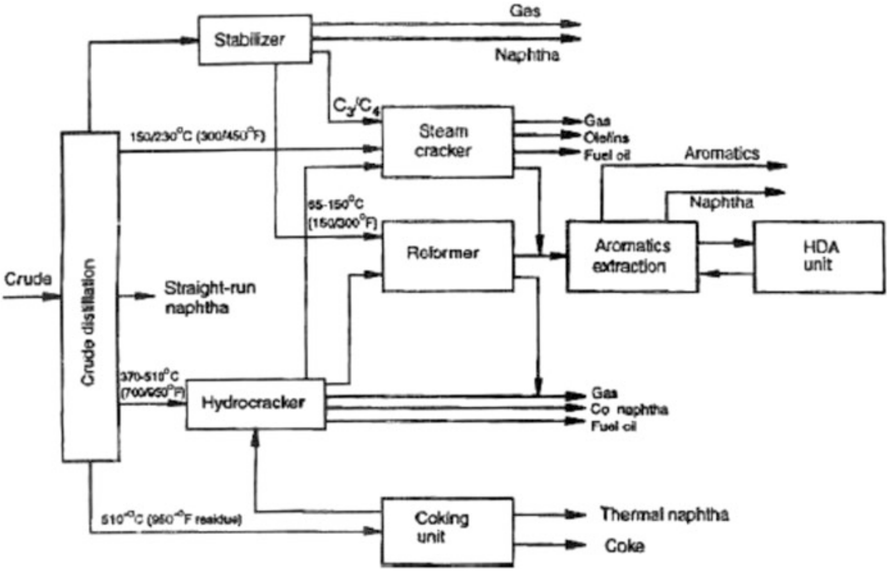


Fig. 17 A petrochemical refinery configuration

Producing the Olefin Feedstock

The source of olefins in a refinery configuration is from either the FCCU, a thermal cracker, or a steam cracker. The olefins produced as a gas are ethylene, propylene, and the C_4s, such as butylenes, butadiene, etc. Liquid olefinic products from these units are normally hydrotreated to make reformer feedstock and thus the BTX feed. All products, of course, are treated for sulfur control and cleaned up before leaving the refinery as petrochemical feedstock. The specifications for these products are stringent and usually the "clean-up" plants are dedicated to the treatment of these products.

Olefins are used mostly in the production of polymers such as the vinyl polymers (vinyl chloride, vinyl acetate, and the like), polyethylene products, and polypropylene products. The heavier C_4s are a major constituent in the production of synthetic rubbers. Figure 17 shows a configuration for a typical petrochemical refinery.

The petrochemical refinery is also further described and discussed in the chapter entitled "▶ Non-energy Refineries in Petroleum Processing."

Appendix 1 Procedure for Manual Calculation of an Equilibrium Flash

The equilibrium flash can be calculated using the composition of the feed mixture and the vapor/liquid equilibrium constant of the components in the mixture. This is expressed by the following equation:

$$L = xf/[1 + (V/L)K] \tag{7}$$

where:

L = Total moles/hr of a component in the liquid phase
xf = Moles/hr of the component in the feed
V/L = Ratio of total moles vapor to total moles liquid
K = Equilibrium constant for each component at the temperature and pressure of the flash

The flash calculations can be done using a process simulation program employing appropriate thermodynamic models or manually using a spreadsheet. There are several publications giving values for K. Among these are the charts in Maxwell's *Data Book on Hydrocarbons* which are based on fugacities. Others may be found in engineering data books such as "Gas Processors Suppliers Association" (GPSA) which are based on convergence pressures. A rough and ready substitute for *K* factors is to use the vapor pressure of the component divided by the system pressure. This, however, should not be used for any definitive design work nor in systems which have azeotropes or are near their critical conditions. A method for calculating equilibrium flash vaporization to produce two, primarily, hydrocarbon, phases is given by the following steps. If significant amounts of water are present, more complex procedures are required. Such a "three-phase" flash with water is not included here.

Note that this procedure can be adapted to provide a simple and useful spreadsheet flash calculation, making use of the iterative calculation option that is available in most spreadsheets.

Step 1. Prepare a table with the first column giving the components making up the feed. The second column will be the composition of the feed in mols/hr. The third column is a listing of the equilibrium constant *K* for each component at the temperature and pressure of the flash condition. Allow up to three columns following for assumptions of *V*/*L*. Each of these three columns should be subdivided into two, the first giving the product of (V/L) *K* and the second for listing the "*L*" for each component. Other columns may be added to calculate mole wt of vapor and SG of the liquid phase.

Step 2. Assume a value for *V*/*L*. This is a judged assumption, but start with 1.0 or 0.1 whichever seems to be more realistic. Calculate (V/L) *K* for each component.

Step 3. Calculate "*L*" for each component from the equation:

$$L = xf\ /[1 + (V/L)K] \tag{8}$$

Step 4. The calculated *V*/*L* is now obtained by adding the "*L*" column and subtracting this value from the total moles of feed in column 1. This subtraction is the vapor moles as calculated. Then the calculated *V*/*L* is arrived at by dividing the total *V* by the total of the "*L*" column.

Table 9

			First trial		Second trail		Third trial					
			V/L guess	0.5	V/L guess	0.2	V/L guess	0.1				
	F, mol/h	K at 127 psia, 300 °F	(V/L) K	L = F/(1 + (V/L) K)	(V/L) K	L = F/(1 + (V/L) K)	(V/L) K	L = F/(1 + (V/L) K)	MW	Liquid lb/h	lb/gal	GPH
C_2	6.4	9.100	4.550	1.153	1.820	2.270	0.910	3.351	30	101	2.97	34
C_3	43.5	5.000	2.500	12.429	1.000	21.750	0.500	29.000	44	1,276	4.69	272
iC_4	16.9	3.300	1.650	6.377	0.660	10.181	0.330	12.707	58	737	4.69	157
nC_4	67.6	2.900	1.450	27.592	0.580	42.785	0.290	52.403	58	3,039	4.87	624
iC_5	80.5	1.800	0.900	42.368	0.360	59.191	0.180	68.220	72	4,912	5.21	943
nC_5	34.6	1.600	0.800	19.222	0.320	26.212	0.160	29.828	72	2,148	5.26	408
C_6	124.9	0.850	0.425	87.649	0.170	106.752	0.085	115.115	86	9,900	5.54	1,787
C_7	140.9	0.480	0.240	113.629	0.096	128.558	0.048	134.447	100	13,445	5.74	2,342
NP260	99.8	0.212	0.106	90.235	0.042	95.741	0.021	97.728	114	11,141	6.18	1,803
NP300	99.8	0.116	0.058	94.329	0.023	97.537	0.012	98.656	126	12,431	6.37	1,951
NP340	60.4	0.063	0.032	58.556	0.013	59.648	0.006	60.022	136	8,163	6.46	1,264
NP382	29.8	0.035	0.018	29.287	0.007	29.593	0.004	29.696	152	4,514	6.56	688
Total	805.1			582.827		680.218		731.172	98.2	71,805	5.85	12,273
Calc V/L				0.276		0.155		0.092			API = 70	

lb/h liquid = 71,805
lb/h vapor = 7,260
lb/h feed = 79,065
lb/gal = 5.9
Liquid mol. wt. = 98.2

Step 5. The calculation is complete when V/L calculated is equal to V/L assumed. An answer within 5 % is usually acceptable. If the calculated V/L assumed is not within this limit, make another assumption for V/L and repeat steps 2, 3, and 4. For this second assumption try 5, or 0.5, or 0.05, whichever is most appropriate.

Step 6. If there is still no agreement between assumed and calculated V/L, plot the two trial points (assumed V s calculated) on log graph paper. Draw a straight line through these two points and note where on this line assumed $V/L =$ calculated V/L. This value is the next assumed V/L. Repeat the calculation steps 2–4 using this value; this usually completes the calculation. If it does not then check that the conditions for the flash are within the boiling point and condensing point for the feed.

In the example below, it is desired to determine the amount of vapor and liquid and their compositions in a feed to a fractionator at 112 psig and 300 °F (Table 9).

Note the components NP260–NP382 are pseudo components having mid-boiling points of 260 °F, 300 °F, 340 °F, and 382 °F respectively. K for these components are based on their vapor pressure and system pressure relationship.

Predicting the EFV Curve from TBP Data. For crude oils and complex mixtures such as the heavy products, the equilibrium vaporization curve can be calculated from the TBP curve using empirical methods given by Edmister or Maxwell. In this work the EFV is based on the method by Maxwell in his book *Hydrocarbon Data*. This method has been described in the section "Developing the TBP Curve and the Equilibrium Flash Vaporization (EFV Curve from the ASTM Distillation Curve" of this chapter.

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