

## DISTILLATION

### Introduction

Refining petroleum involves subjecting the feedstock to a series of physical and chemical processes as a result of which a variety of products are generated. In some of the processes, e.g., distillation, the constituents of the feedstock are isolated unchanged, whereas in other processes, e.g., cracking, considerable changes are brought about to the constituents. Recognition that refinery behaviour is related to the composition of the feedstock has led to a multiplicity of attempts to establish petroleum and its fractions as composition of matter. As a result, various analytical techniques have been developed for the identification and quantification of every molecule in the lower boiling fractions of petroleum. It is now generally recognized that the name petroleum does not describe a composition of matter but rather a mixture of various organic compounds which includes a wide range of molecular weights and molecular types that exist in balance with each other (Speight, 1994; Long and Speight, 1998). There must also be some questions of the advisability (perhaps futility is a better word) of attempting to describe every molecule in petroleum. The true focus should be to what ends these molecules can be used.

Thus, investigations of the character of petroleum need to be focused on the influence of its character on refining operations and the nature of the products that will be produced. Further, one means by which the character of petroleum has been studied is through its fractional composition. However, the fractional composition of petroleum varies markedly with the method of isolation or separation, thereby leading to potential complications (especially in the case of the heavier feedstocks) in the choice of suitable processing schemes for these feedstocks. Crude oil can be fractionated into three or four general fractions: (1) asphaltene fraction, (2) resin fraction, (3) aromatics fraction, and (4) saturates fraction. Thus, it is possible to compare interlaboratory investigations and hence to apply the concept of predictability to refining sequences and potential products. Investigations of the character of petroleum through fractionation studies has been practised for more than 170 years (Boussingault, 1837), although modern fractionation techniques are essentially a twentieth-century approach to examining petroleum composition (Rostler, 1965; Altgelt and Gouw, 1979). In fact, the fractionation of petroleum has evolved to such an extent that it is now possible to determine with a high degree of accuracy, the types of compounds present in crude oil. The fractionation methods available to the petroleum industry allow a reasonably effective degree of separation of hydrocarbon

mixtures. However, the problems are separating the petroleum constituents without alteration in their molecular structure and obtaining these constituents in a substantially pure state.

## DISTILLATION

Distillation is a means of separating chemical compounds (usually liquids) through differences in their vapor pressures. The theory of distillation has occupied several large texts and is discussed only briefly here (Halvorsen and Skogestad, 2000; Petyluk, 2004; Lei et al., 2005). Simple distillation is effective only when separating a volatile liquid from a non-volatile substance or when separating two liquids that differ in boiling point by 50°C or more. If the liquids comprising the mixture that is being distilled have boiling points that are closer than 50°C to one another, the distillate collected will be richer in the more volatile compound, but not to the degree necessary for complete separation of the individual compounds. Thus, in the mixture, the components evaporate and the vapor has a composition determined by the chemical properties of the mixture. Distillation of a given component is possible, if the vapor has a higher proportion of the given component than the mixture. This is caused by the given component having a higher vapor pressure and a lower boiling point than the other components. The minimum in distillation is flash distillation, where either the temperature is rapidly increased or pressure reduced, and vapor and liquid fractions are thus obtained, which may be processed as such. The device used in distillation is referred to as a still and consists of a minimum of a reboiler (pot) in which the source material is heated, a condenser in which the heated vapor is cooled back to the liquid state, and a receiver in which the concentrated or purified liquid is collected. The equipment may affect separation by one of two main methods. First, the vapors given off by the heated mixture may consist of two liquids with significantly different boiling points. Thus, the vapor that is given off is a vast majority of one or the other liquid, which after condensation and collection effects the separation. Second, fractional distillation may be necessary and is more effective at separating liquids that have similar boiling points. This method relies on a gradient of temperatures existing in the condenser stage of the equipment. Often in this technique, a vertical condenser, or column, is used and by removal of the distillation products that are liquid at different heights up the column, it is possible to separate liquids that have different boiling points. The greater the distance over which the temperature gradient in the condenser is applied, the easier and more complete the separation.

The basic idea behind fractional distillation is the same as simple distillation, only the process is repeated many times. If simple distillation was performed on a mixture of liquids with similar volatilities, the resulting distillate would be more concentrated in the more volatile compound than the original mixture, but it would still contain a significant amount of the higher boiling compound. If the distillate of this simple distillation was distilled again, the resulting distillate would again be even more concentrated in the lower boiling compound, but still a portion of the distillate would be the higher boiling compound. If this process is repeated several times, a fairly pure distillate will eventually result. This, however, would take a very long time. In fractional distillation, the vapors formed from the boiling mixture rise into the fractionating column where they condense on the column's packing. This condensation is tantamount to a single run of simple distillation; the condensate is more concentrated in the lower boiling compound than the mixture in the distillation flask. As vapors continue to rise through the column, the liquid that has condensed will vaporize. Each time this occurs, the resulting vapors are more and more concentrated in the more volatile substances. The length of the fractionating column and the material it is packed with, impact the number of times the vapors will condense before passing into the condenser; the number of times the column will support this is referred to as the number of theoretical plates of the column.

Types

1.

#### ATMOSPHERIC PRESSURE

Distillation is a common method for the fractionation of petroleum that is used in the laboratory as well as in refineries. The technique of distillation has been practised for many centuries and it was recognized in the early days of the refining industry, that the desirable product (kerosene as a lamp oil) could be separated by distillation. Thus, it is not surprising that distillation became the process of choice for petroleum refining and the process has evolved from the simple distillation units to the complex multiplate still used in the refining industry. Distillation has found wide applicability in petroleum science and technology, but it is generally recognized that the fractions separated by distillation are only rarely, if at all, suitable for designation as a petroleum product. Each usually requires some degree of refining, which of course varies with the impurities in the fraction and the desired properties of the finished product. Nevertheless, distillation is the most important fractionating process for the separation of petroleum hydrocarbons; it is an essential part of any refinery operation (Bland and Davidson, 1967). However, insofar as petroleum is a mixture of several thousand (or even more) individual chemical compounds, there is little commercial emphasis on the

isolation of the individual components. The aim of the distillation of petroleum is predominantly an assessment of the nature and volatility of the material through separation into several fractions of substantially broad boiling ranges. The initial fractionation of crude oil essentially involves distillation of the material into various fractions, as illustrated by the distillation procedure used for the boiling range specifications of petroleum (Chapter 8). The fractions into which crude oil is commonly separated do vary depending on the nature and composition of the crude oil; indeed, as the terminology indicates, there is considerable overlap between the various fractions. The kerosene (stove oil) and light gas oil fractions are often referred to as middle distillates and usually represent the last fractions to be separated by distillation at atmospheric pressure. This leaves the fractions from the heavy gas oil and higher boiling material that are collectively called reduced crude.

An atmospheric distillation unit (atmospheric pipe still) is a distillation unit that contains a large number of theoretical plates, and the side streams are taken off at different heights up the distillation tower. The petroleum is partially or totally vaporized in a furnace and then fed to the bottom of the atmospheric still. The distillation tower separates the petroleum by boiling point, i.e., molecular weight, with the lower molecular weight more volatile constituents concentrating at the top of the column and the higher molecular weight less volatile constituents concentrating at the bottom of the column. Naphtha is the chemical precursor of gasoline and boils over the same range, while the atmospheric residuum has an initial boiling point on the order of 350 °C (660 °F). The atmospheric residuum can be distilled further in a vacuum distillation unit.

#### REDUCED PRESSURES

Separation of the reduced crude into the constituent fractions requires that the next-stage distillation be carried out under reduced pressure. The higher boiling constituents undergo thermal decomposition at temperatures above 350 °C (660 °F). This will result in molecular fragmentation leading to volatile products (that were not indigenous to the crude oil) and to coke. To avoid these thermal reactions, it is necessary to reduce the pressure at which distillation is performed, and since the vapor pressure and temperature are related, the lowering of pressure is accompanied by a corresponding decrease in the boiling points of the individual constituents. For example, a specific compound boiling near 350°C (660°F) at 1 atm (760 mm Hg) may boil over 100 °C (180°F) lower (approximately 250°C, 480 °F) at 25 to 30 mm Hg, and the danger of thermal decomposition, as with the other thermal interactions, is markedly reduced, if not eliminated.

The vacuum distillation unit (vacuum pipe still) is a distillation unit that contains a smaller

number of theoretical plates than the atmospheric distillation unit and, again, the side streams are taken off at different heights up the distillation tower. The atmospheric residuum is fractionated to produce overhead fractions such as vacuum gas oils and lubricating oil distillates, and the bottoms is a vacuum residuum with an initial boiling point of about 565°C (1050°F), calculated to atmospheric pressure. The amounts of the various fractions obtained by distillation depend on the nature of the crude oil, which is reflected in the boiling point profile. Clearly, petroleum character is very important to the refiner in meeting the product demands of customers as well as in determining what further processing the distillation products may require. For example, the distillates from one crude oil (e.g., Louisiana crude oil) are suitable feedstocks for lubricating oils and specialty products. On the other hand, the distillates from another crude oil (e.g., Bachaquero crude oil) are more suitable for use as fuel oil. Thus, the boiling range of petroleum along with its quality is so important to a refiner in meeting the product slate that most refineries must be able to meet any changes in feedstock quality by adapting the refining options. In the laboratory (but not always practical in the refinery), lower pressures can be attained by use of an empty column or a spinning band column. With these, the pressure drop is small enough that low pressures can be maintained in the reboiler. For instance, with a distillate pressure of 0.1 mm Hg, one may have a pressure of 0.5 to 1 mm Hg in the reboiler that, theoretically, allows the collection of distillates with an atmospheric equivalent temperature cut point of as high as 560°C (1050°F). The actual observed boiling points during this distillation are, of course, much lower. Despite the low pressure, the reboiler may have to be heated as high as 370°C (700°F) for such high-boiling distillates. From the actual boiling points obtained at reduced pressure, the so-called atmospheric equivalent temperatures (AET) are calculated at which the material would boil under atmospheric pressure.

## **AZEOTROPIC AND EXTRACTIVE DISTILLATION**

Chemical bonding between the components of the mixture creates properties unique to the mixture. If the system forms azeotropes, as in a benzene and cyclohexane system, a different problem arises—the azeotropic composition limits the separation, and for a better separation this azeotrope must be bypassed in some way. At the azeotropic point, the mixture contains the given component in the same proportion as the vapor, so that evaporation does not change the purity, and distillation does not affect separation. For example, ethyl alcohol and water form an azeotrope (azeotropic mixture) at 78.2°C. If the separation of individual components from petroleum itself or from petroleum products is required, there are means by which this can be

accomplished. For example, when a constant-boiling mixture of hydrocarbons contains components whose vapor pressure is affected differently by the addition of, say, a nonhydrocarbon compound, distillation of the hydrocarbon mixture in the presence of a nonhydrocarbon additive may facilitate separation of the hydrocarbon components. In general, the nonhydrocarbon additive is a polar organic compound and should also have the ability to form a binary minimum constant-boiling (or azeotropic) mixture with each of the hydrocarbons. Thus, it is often possible to separate compounds that have very close boiling points by means of azeotropic distillation. However, when the added compound is relatively nonvolatile, it exists almost entirely in the liquid phase, and the process is actually extractive distillation.

Therefore, extractive distillation is distillation in the presence of a miscible, high boiling, relatively non-volatile component, the solvent, which forms no azeotropes with the other components in the mixture. It is widely used in the chemical and petrochemical industries for separating azeotropic (close boiling) and other constituents in a mixture. In extractive distillation, the solvent is specially chosen to interact differently with the components of the original mixture, thereby altering their relative volatility. Because these interactions occur predominantly in the liquid phase, the solvent is continuously added near the top of the extractive distillation column so that an appreciable amount is present in the liquid phase on all of the trays below. The mixture to be separated is added through second feed point further down the column. In the extractive column, the component having the greater volatility, not necessarily the component having the lowest boiling point, is taken overhead as a relatively pure distillate. The other component leaves with the solvent via the column bottoms. The solvent is separated from the remaining components in a second distillation column and then recycled back to the first column. The separation of petroleum by distillation into fractions results in a concentration effect in which the heteroatom constituents (metals included) occur for the most part in the residua.

## **SOLVENT TREATMENT**

The use of solvents invokes the concept of the solubility (or insolubility) of a solute in the chosen solvent. The solubility of a solute is the maximum quantity of solute that can dissolve in a certain quantity of solvent or quantity of solution at a specified temperature. The main factors that have an effect on solubility are: (1) the nature of the solute and solvent, (2) temperature, and (3) pressure. The rate of solution is a measure of how fast a substance dissolves. Some of the factors determining the rate of solution are: (1) size of the particles, (2)

stirring, (3) the amount of solute already dissolved, and (4) temperature. In order for a solvent to dissolve a solute, the particles of the solvent must be able to separate the particles of the solute and occupy the intervening spaces. Polar solvent molecules can effectively separate the molecules of other polar substances. This happens when the positive end of a solvent molecule approaches the negative end of a solute molecule. A force of attraction then exists between the two molecules. The solute molecule is pulled into solution when the force overcomes the attractive force between the solute molecule and its neighboring solute molecule. Ethyl alcohol and water are examples of polar substances that readily dissolve in each other. Polar solvents can generally dissolve solutes that are ionic. Fractionation of petroleum by distillation is an excellent means by which the volatile constituents can be isolated and studied. However, the nonvolatile residuum, which may actually constitute from 1% to 60% of the petroleum, cannot be fractionated by distillation without the possibility of thermal decomposition, and as a result, alternative methods of fractionation have been developed. The distillation process separates light (lower molecular weight) and heavy (higher molecular weight) constituents by virtue of their volatility and involves the participation of a vapor phase and a liquid phase. These are, however, physical processes that involve the use of two liquid phases, usually a solvent phase and an oil phase.

Solvent methods have also been applied to petroleum fractionation on the basis of molecular weight. The major molecular weight separation process used in the laboratory as well as in the refinery is solvent precipitation. Solvent precipitation occurs in a refinery in a deasphalting unit and is essentially an extension of the procedure for separation by molecular weight, although some separation by polarity might also be operative. The deasphalting process is usually applied to the higher molecular weight fractions of petroleum such as atmospheric and vacuum residua for the production of asphalt or demetallized deasphalted oil.