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PETROLEUM REFINERY DISTILLATION

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R.N. Watkins
Sugar Land, Texas
January 2, 1973

contents

introduction

This book was written to fill a void which exists in the technical literature which the author encountered early and often in his career. Although petroleum distillation has been practiced for over a century, there has been precious little published literature in the field. In the field of articles, Packie's (1) classical work has been, up to this very day, the first and best basic. Later work by Prater and Boyd (2) and by Watkins (3) completes the existing short articles available. In textbooks, a brief treatment by Nelson (4) and by van Winkle (5) is all that one can locate as reference material. The situation is not much better in the private confidential literature.

Several years ago, I joined a major engineering-construction firm after having spent over six years in the petrochemical industry. At that time, my practical knowledge of petroleum processing was slight. As luck would have it, I was soon called upon to design a petroleum-processing tower. After receiving brief and very general guidelines, I got underway. My first approach was to seek help from more experienced men in the firm. At this point, I received the shock of my life. Since this particular tower was a little different from the conventional oil plant, no one could be very helpful because, while they might have worked previously on a refinery design, they were not particularly knowledgeable about the variables one must consider in petroleum distillation. And so, I turned to the literature—and found nothing. The library is full of books covering distillation—theory, practice, equilibrium, equipment design and every other conceivable topic. Trade journals continue to carry "new and improved" calculation techniques for conventional distillation. Why so little on petroleum fractionation? I suspect that the answer to this question lies in two areas. First, until Edmister's book (6) appeared in 1961, there were no easy-to-use correlations for vapor-liquid equilibrium in heavy oils. Secondly, many engineers today are more interested in studying computer solutions of engineering problems wherein the method of solving the problem is the primary concern followed at a discrete distance by the consideration of the chemical engineering fundamentals involved.

This book is intended to be, first of all, practical and usable by the working engineer and is primarily addressed to him. Secondarily, it is intended to present and, where needed, to clarify proven principles and methods relating to petroleum distillation. It is a fact that techniques in this area of technology and much of the available design data are largely empirical, but, considering that petroleum is a mixture of a very large number of individual components of many different types, how could one expect otherwise? While it would be highly desirable to be able to analyze petroleum distillation with the same degree of clarity and knowledge as one might the separation of ethyl alcohol and water, it is unreasonable to demand such approaches to these problems. Empiricism, while often an anathema to the academic scholar, does provide the man in the field with working solutions to his daily problems. Empirical

methods have yet another asset and one not always true of theoretical explanations–they work–for they rationalize and attempt to explain observed phenomena which have resisted substantiation by theory.

As in any technical book being written today, there is little that can be claimed as radically new. Much of the new data and methods being made available today are in the form of articles in journals or papers delivered at symposia. What is new about this book is that it assembles in one place for the first time in the public literature a complete set of design/analytical procedures for every type of fractionation process to be found in a modern petroleum refinery or petrochemical plant. These procedures are those currently in use throughout the industry and have been proven by performance.

The book is organized into chapters, each one describing in detail a particular type of distillation process and the applicable design procedures. Illustrative material is provided where required to clarify the narrative material. As to the sources of data used in developing the calculations and design correlations, The American Petroleum Institute–the API–has published a data book (7) which contains its recommendations as to the best methods available in the public domain for estimating physical properties of petroleum and petroleum fractions. Nelson and Maxwell (8) are also valuable sources of such data. For heavy oil vapor-liquid equilibrium calculations, the methods of Packie and Edmister are in general use. In the example calculations, the thermal data was that of Johnson and Grayson (9).

Please note that in many places, the narrative material refers to the "owner." The "owner" is defined as the party ultimately responsible for the acceptance and operation of the facilities under study. Many basic decisions at the beginning of a design should be made by the person who is ultimately going to be responsible for the operation of the unit even though many routine decisions must still be made by the process designer in the course of the job.

It is assumed by the author that the reader has a basic understanding of distillation, of crude petroleum of petroleum products and their specifications and of petroleum refinery processes. If this is not the case, he is referred specifically to Nelson and to Hengstebeck (10) for background information.

As a final word of explanation and caution, the methods presented in this book are not intended as *the one, only, sacred way to do it.* These procedures have been developed by the author as logical approaches to solving problems and represent one man's experience and opinions. The reader is encouraged to examine these methods critically in the light of his own experiences and to govern himself accordingly.

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atmospheric tower

Crude petroleum as it is produced from the field is a relatively low-value material since, in its native state, it is rarely usable directly. However, it can be refined and further processed into any number of products whose value is many times that of the original oil. The first step in any petroleum refinery is the separation of the crude into various fractions by the process of distillation. These fractions may be products in their own right or may be feedstocks for other refining or processing units.

In most refineries, this process is carried out in two stages. The oil is first heated to the maximum temperature allowable for the crude being processed and for the operation being practiced and then fed to a fractionating tower which operates at slightly above atmospheric pressure. This tower is usually called the *atmospheric tower*. It yields several distillate products and a bottoms product which is the residual liquid material which could not be vaporized under the conditions of temperature and pressure existing in the atmospheric tower. This bottoms liquid is then reheated to the maximum allowable temperature—usually higher than the maximum temperature allowed for the feed to the atmospheric tower—and fed to a fractionating tower which operates at subatmospheric pressure. This tower is usually called the *vacuum tower*. This chapter describes the atmospheric tower. The vacuum tower is discussed in Chapter 3.

Although the process of crude oil distillation has been practiced in the United States for more than 100 years, the design and operation of these units is still accomplished almost exclusively on an empirical and, in some cases, even a nearly emotional basis. This is undoubtedly due to the fact that crude oil is made up of an almost infinite number of discrete hydrocarbons, all the way from methane to materials having 70 or more carbon atoms.Thus, the process and/or its products are usually discussed in terminology which is unique to the petroleum industry. In this introductory material, the nomenclature usually employed in crude oil distillation will be discussed before proceeding into the design methods.

Analysis of Crude Petroleum and Its Fractions

A complete component-by-component analysis of a crude oil sample is not practically realizable. For this reason, the composition of any given oil is approximated by a *true boiling point* distillation, commonly called TBP distillation. A thorough discussion of the equipment and procedures involved is given in Chapter 4 of Nelson (1). This method is basically a batch distillation using a large number of stages and a high reflux-to-distillate ratio so that the temperature at any point on the temperature-volumetric yield curve represents the actual (true) boiling point of the hydrocarbon material present at the volume percentage point.

TBP distillations are normally run only on crude oils and not on petroleum fractions. Instead, a rapid distillation procedure is used for analysis of petroleum products and

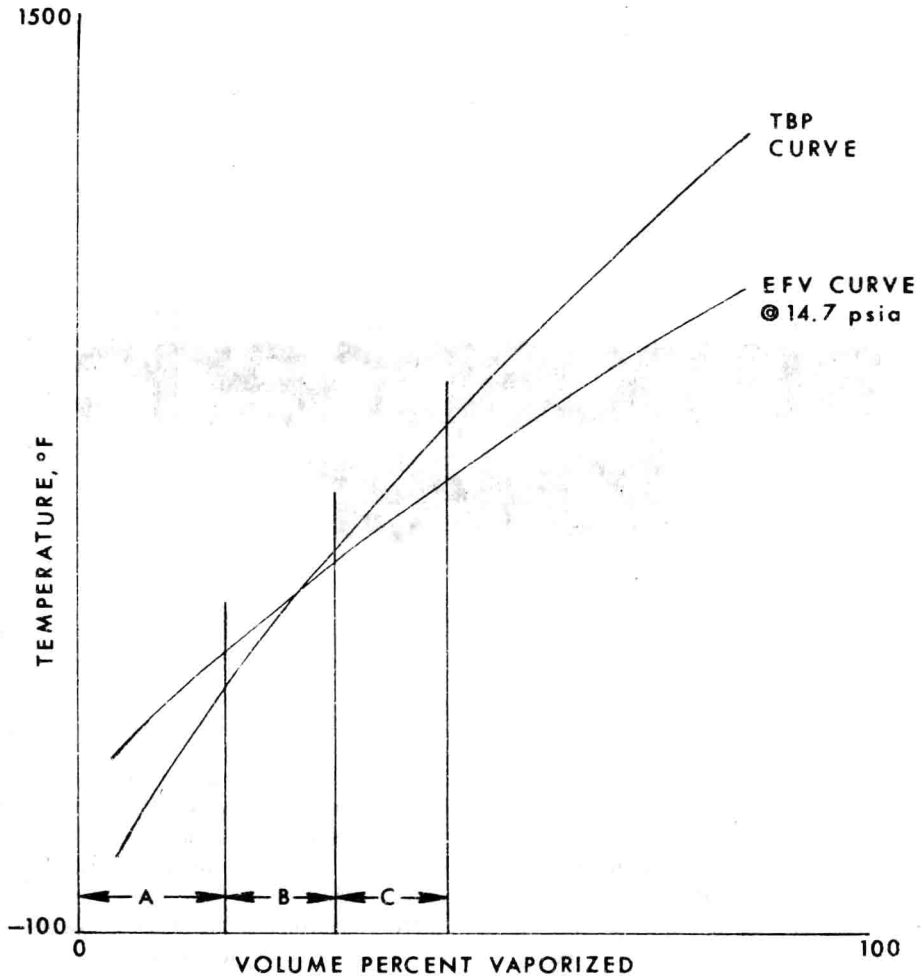

Figure 2.1. TBP and EFV Curves for a typical crude oil and product yield by volume.

intermediate fractions. These procedures were developed by the American Society for Testing Materials and are called ASTM distillations. These methods are rapid batch distillations employing no trays or reflux between the stillpot and the condenser. The only reflux available is that generated by heat losses from the apparatus. These test methods are used in control laboratories throughout the world.

The third type of laboratory distillation which is used in discussing petroleum fractionation is the *equilibrium flash vaporization* (distillation) commonly called the EFV. The procedure is also discussed in Chapter 4 of Nelson. This distillation can be run at pressures above atmospheric as well as under vacuum, whereas the TBP and ASTM distillations are run either at atmospheric pressure or under vacuum. EFV curves are seldom run because of the time and expense involved and are almost exclusively limited either to crude oil or to reduced crude samples (atmospheric tower bottoms liquid) which are being evaluated as vacuum tower charge stocks. The EFV initial boiling point is the bubble point of the fraction under study, and the EFV final boiling point is its dew point. If desired, a family of EFV curves can be run at a series of pressures encompassing the envisioned operating pressure. This will allow a more accurate estimate of phase behavior than can be attained from calculations.

The purpose for running these various distillations is to characterize the composition of the material under study, and, for this reason, the boiling range of petroleum liquids is of primary importance. For example, kerosene will have an ASTM boiling range of approximately 325 to 525 degrees F which corresponds to a TBP boiling range on the order of 275 to 575 degrees F. While the latter is theoretically indicative of actual composition, the former is the one used by both designers and operators in discussing distilla-

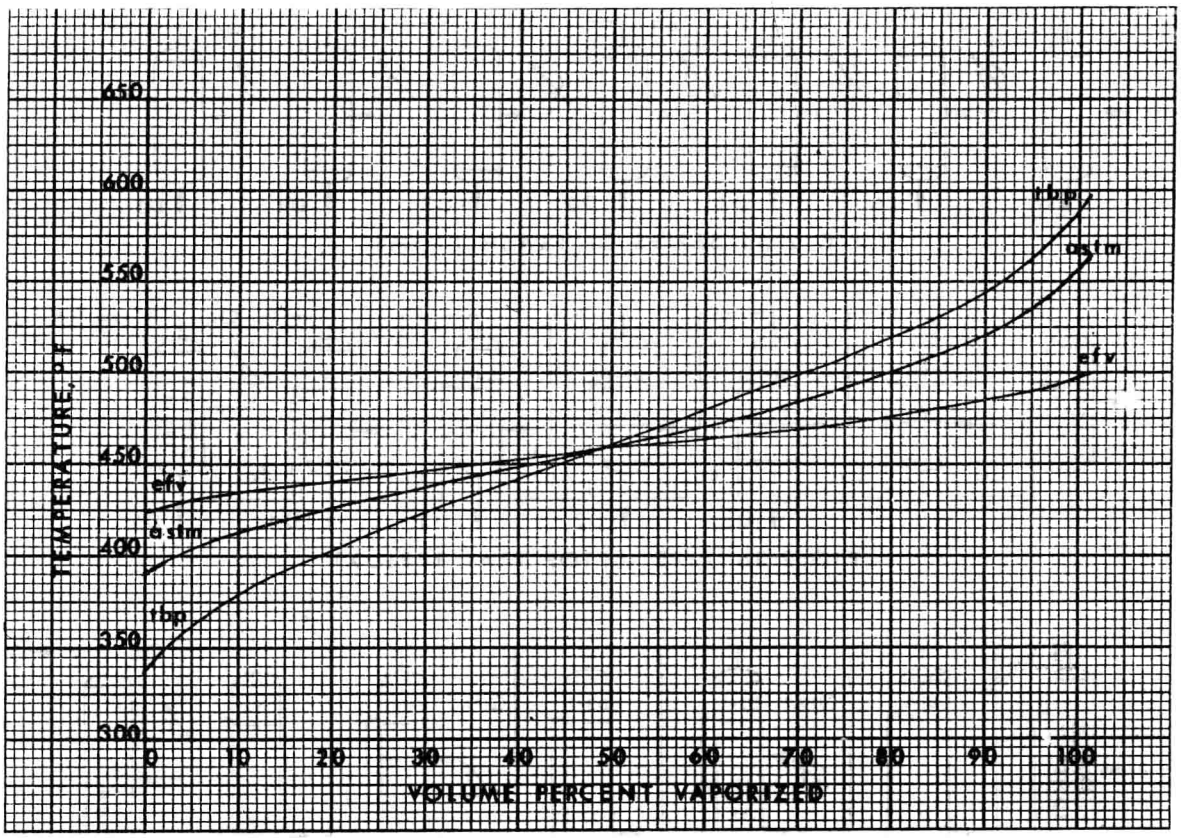

Figure 2.2. ASTM, TBP and EFV curves for 39.7 degree API light distillate.

tion problems. The EFV curve is used for determining phase behavior of liquids and, thus, is usually of interest principally to designers.

Figure 2.1 shows the TBP and atmospheric pressure EFV curves for a typical crude oil. Also illustrated is the planned yield of three distillate products for a process under study. Figure 2.2 shows the ASTM, TBP and atmospheric EFV distillation curves for a typical petroleum fraction.

The complete and definitive analysis of a crude oil, usually called a *crude assay*, is considerably more detailed than a TBP curve and a whole crude API gravity. A complete crude assay will contain some or all of the following:

1. Whole crude gravity, viscosity, sulfur content, pour point, etc.
2. TBP curve, mid-volume plot of gravity, viscosity, sulfur, etc.
3. Light-ends analysis up through C_8 or C_9.
4. Properties of fractions (naphthas, middle distillates, gas oils and residua)—yield as volume percent, gravity, sulfur, viscosity, octane number, diesel index, flash and fire point, freeze point, smoke point, pour point, vapor pressure, etc.
5. Properties of lube distillates (only if the crude is suitable for the manufacture of lube basestocks).
6. Properties of asphalts (only if the residua have suitable characteristics for preparation of asphalts).
7. Detailed studies of fractions for various properties, e.g., octane number versus yield for naphthas or viscosity versus yield for lubestocks.
8. EFV curve run at atmospheric pressure and/or phase diagram, although this is rarely done.

Much of this information is of little use in design work but is of great importance to the refiner or to a crude oil purchaser.

A typical assay of a commercial crude oil is included in the Appendix. This data was developed experimentally and correlated by Humble Oil & Refining Company and is reproduced here with their permission.

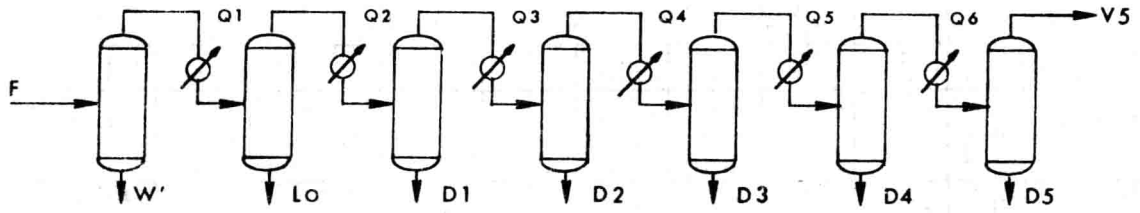

FIG. 2-3a - SERIES OF FLASH DRUMS

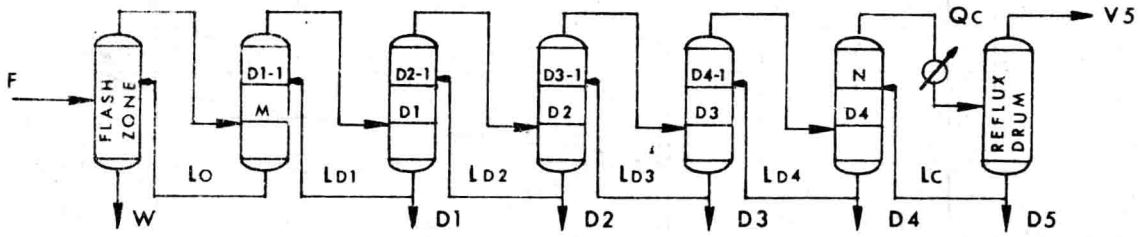

FIG. 2-3b - TYPE U (TOP TRAY REFLUX)

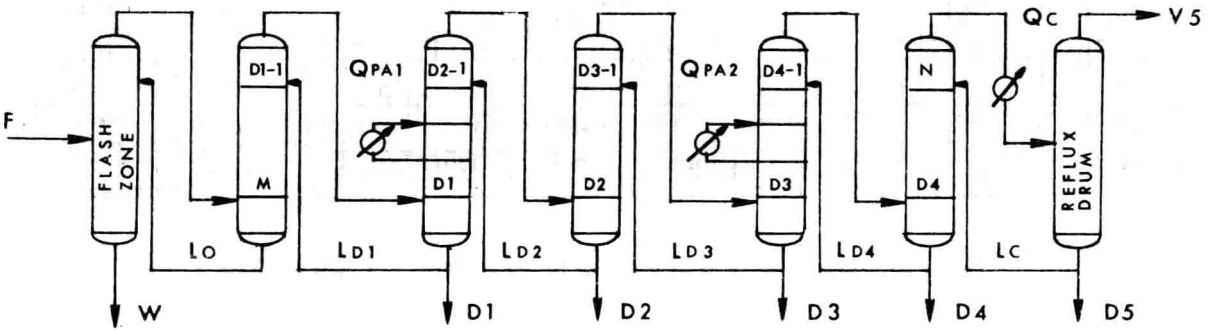

FIG. 2-3c - TYPE A (PUMPAROUND REFLUX)

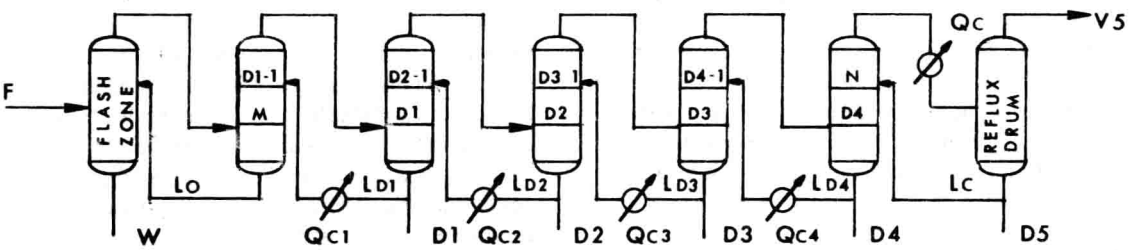

FIG. 2-3d - TYPE R (PUMPBACK REFLUX)

Figure 2.3. Processing schemes for atmospheric distillation of crude oil.

Basic Processes for Atmospheric Crude Distillation

The distillation of crude petroleum into fractions having different properties is similar to many more familiar types of fractionation processes although, on the surface, this may not appear to be so. In order to avoid details which are of only secondary importance at this point and to get down to the basics of the problem, the separation of crude oil into its desired fractions will be considered separately, disregarding the effect of sidestream product and bottoms liquid stripping, either by steam or by reboiling in the case of the lighter sidestreams. Further, the separation will

be defined as five distillate fractions and a residual (bottoms) liquid. The lightest distillate fraction is not always completely condensible at the conditions of temperature and pressure in the reflux drum and, thus, may be yielded as two distillate fractions, one vapor and one liquid. A small amount of extra vaporization, called overflash, will be employed to provide adequate reflux in the section between the flash zone, i.e., the point in the tower where the partially vaporized feed enters, and the first (lowest) sidestream product draw tray.

Because of the continuously increasing temperature of crude oil as more and more of the material is vaporized and because the charge is usually heated to its maximum allowable temperature prior to entering the tower, it is not feasible to use a reboiler in crude distillation. Thus, all distillate products plus the overflash must be vaporized up from the flash zone. Another way of stating the same principle is that the total heat input required by the process must be contained in the feed as it leaves the crude furnace.

Figure 2.3 illustrates various processes for yielding distillates from the feed. The nomenclature used in designating the three methods of refluxing the process is the author's own for the purposes of this discussion and has no significance in the petroleum industry. By way of explanation, Type U employs only top tray reflux from an overhead condenser for total process heat removal. Type A employs an externally circulated and cooled stream, called *pumparound reflux*, at one or more side points on the tower for partial process heat removal. Type R employs subcooling of true equilibrium reflux, called *pumpback reflux*, for partial process heat removal, this usually occurring at all sidestream product draw points. In both Type A and Type R, only a portion of the total heat removal can be accomplished by these techniques; the remaining portion of the removal must be satisfied by reflux from the condenser to the top tray.

For the sake of simplicity in discussing Figure 2.3, it is stipulated that the volumetric yield of each product from the crude feed will be the same, regardless of the method used for heat removal.

Consider Figure 2.3*a* as the first method for yielding the desired product pattern. The vapor-liquid mixture from the furnace enters the first flash drum where the residual liquid, W′, drops out. The first drum effluent vapor is cooled just enough to condense the overflash, L_0, and then enters the second drum where this vapor-liquid separation occurs. Although not shown on the sketch, L_0 combines with W′ to form the total residual liquid, W. The vapor is cooled again to some predetermined temperature and enters a third flash drum where D1 separates out. This process is repeated as D2, D3 and D4 are condensed and separated out. The overhead vapor from the sixth drum is cooled to as low a temperature as is possible consistent with the available cooling medium in order to maximize distillate liquid recovery in D5. The noncondensibles form the distillate vapor, V5. Each of these separations has occurred due to cooling and equilibrium condensation so that the liquid from each stage contains appreciable amounts of components lighter than the desired distillate. The equilibrium vapor also contains some of the components which should be in the liquid so that the next fraction to be condensed will have some undesirable heavy ends. All these fractions are portions of a continuum which indicates that it would be possible to use reflux to wash back the heavy components from the vapor and stripping vapors to remove light components from the sidestream products.

Figure 2.3*b* illustrates a Type U system, the first approach to genuine fractionation. Each one of the vessels in the flow line represents one separation section. This type of unit is obviously impractical since heat is removed only in the overhead condenser at a temperature level too low for recovery of heat. Secondarily, the vapor and liquid traffic throughout the column increases markedly from bottom to top, which requires sizing the tower based on flows existing at the top tray. As will be seen later, this will result in a much larger tower diameter than for either Type A or Type R unit. Figure 2.4*a* illustrates the flows around a Type U section. Inspection of the flow scheme reveals that this is merely a conventional rectifying column.

Heat removal at intermediate points on the tower can be attained by withdrawing an internal liquid stream from the tower, cooling it and returning it to the column. The cooling medium is usually the crude oil charge which is being preheated before entering the furnace. Thus, a dual benefit is realized. This can be done in one of two ways.

The more common of the two processes is by the use of pumparound reflux which the author calls a Type A system. This is illustrated by Figures 2.3*c* and 2.4*b*. Liquid is withdrawn from a tray above the lower draw, cooled and returned to a tray further up in the tower but below the upper draw tray. In normal practice, such a section generally uses two or three actual trays including the pumparound draw tray and the tray on which the cooled liquid reenters the tower. This technique is generally employed at a low and at an intermediate point in the tower and makes heat available for exchange against crude oil charge at two different temperature levels. This method has the advantage of stabilizing vapor and true reflux liquid flow throughout the section where it is used as well as significantly reducing vapor and liquid traffic throughout the column. The disadvantage of this method is that the three trays normally used for heat removal must be considered as only one actual tray for fractionation purposes. This is because that, from an equilibrium viewpoint, the pumparound liquid is foreign to the zone in which it is employed. This process is analagous to removing heat from an absorber by withdrawing part of

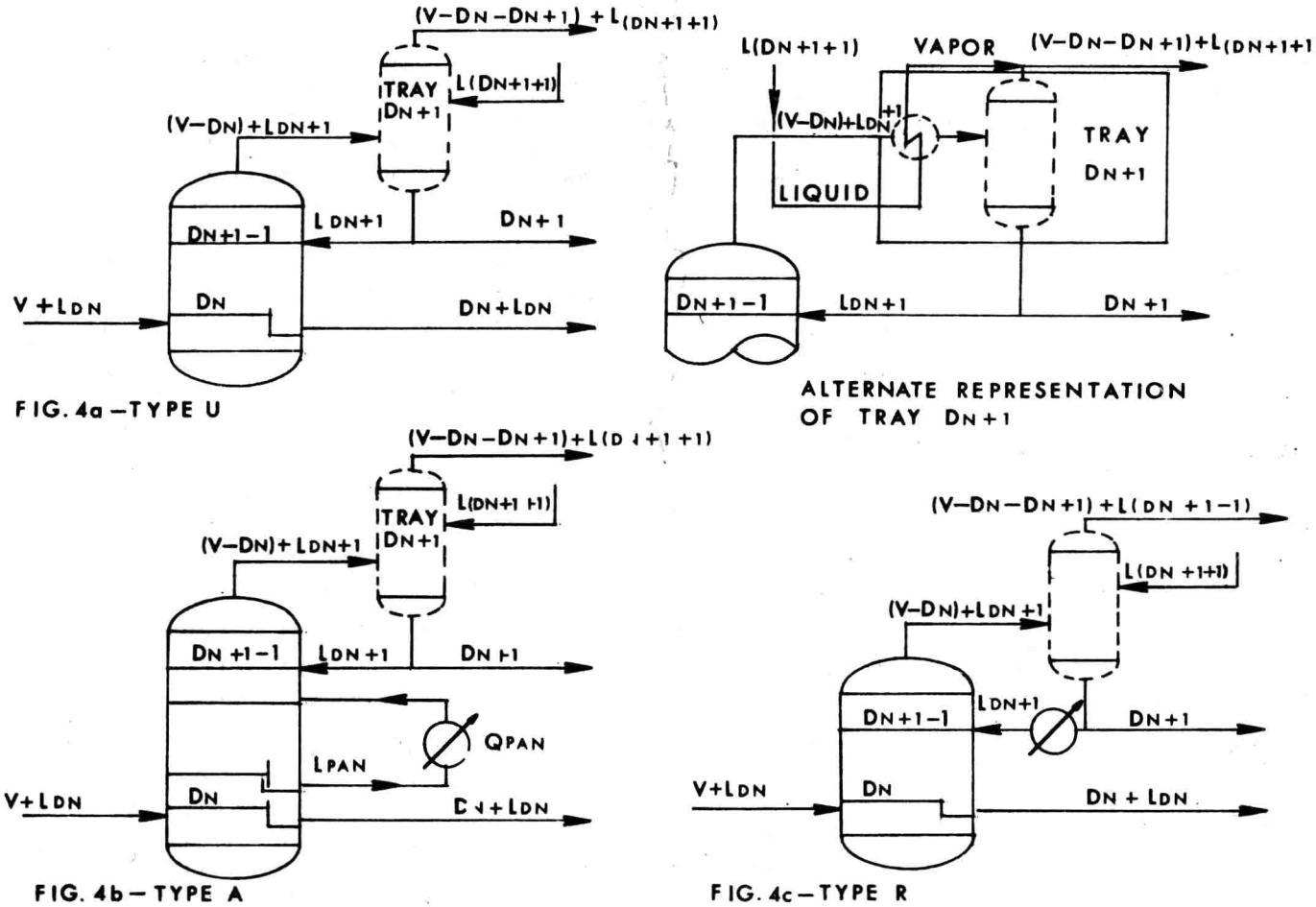

Figure 2.4. Detailed flows around a section for Types U, R and A atmospheric towers.

the bottoms, cooling it and returning it to an upper tray. This is fine for heat removal purposes but penalizes mass tranfer.

Figures 2.3*d* and 2.4*c* show a Type R system which is a rectifying section employing subcooled reflux. The most economical Type R design uses crude oil charge as the cooling medium for the pumpback reflux streams and, thus, also obtains the benefit of feed preheat. Type R is employed at all draw trays. There is the additional advantage that all liquids within the tower are true equilibrium reflux liquids, and, thus, all trays can be considered as being effective for fractionation purposes. A fairly uniform vapor and liquid traffic exists in all sections of the tower.

The typical vapor and liquid traffic which exists in the three types of refluxed columns is shown in Figure 2.5. Note that the Type U tower has continuously increasing vapor and liquid rates while the rates in both the Type A and Type R towers are more or less stabilized by the external heat removal.

Separation Criteria in Petroleum Fractionation

In the context that most chemical engineers apply to distillation of systems made up of discrete compounds identifiable by name, heavy oil fractionation is a black art, especially when encountered for the first time. Over the years, many excellent methods have been published for calculating all types of distillation systems involving discrete compounds. Even the inexperienced engineer is familiar with many of the basic techniques. Petroleum fractionation is quite a different story since the methods of analysis are largely empirical or are based on empirical criteria. However, there is a similarity between light hydrocarbon fractionation and crude oil distillation. It is the purpose of the following to demonstrate this similarity.

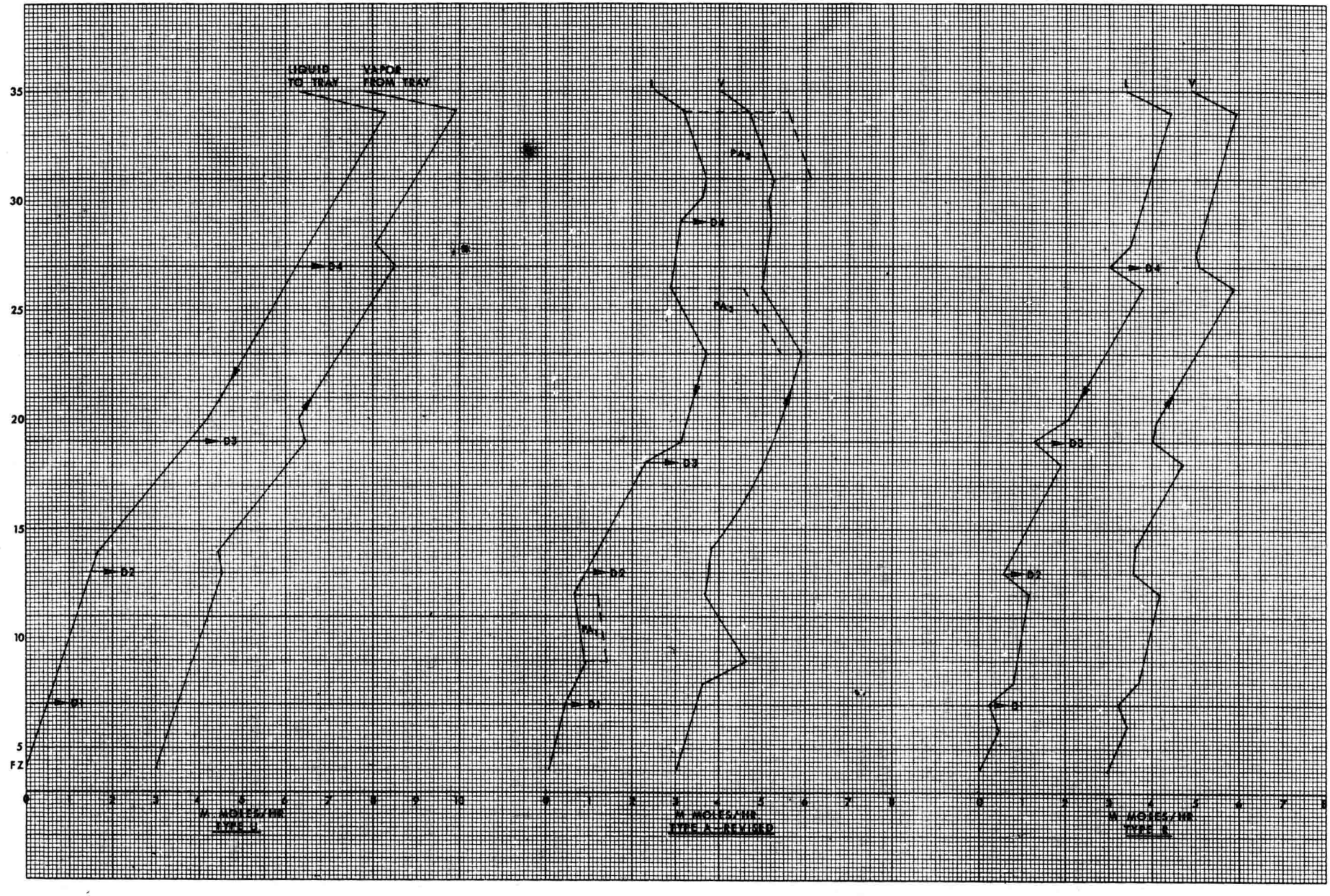

Figure 2.5. Vapor and liquid traffic for Types U, R and A atmospheric towers.

A typical light hydrocarbon separation is that of fractionating between propane and n-butane. This problem requires that the designer provide a sufficiency of trays and reflux to satisfy the composition specifications. Satisfying the trays-reflux requirements depends upon the specified separation requirements of the process and the inherent physical chemistry of the system involved. Talking in terms of a binary system, two terms which will be used later to clarify the language used in heavy oil work must be defined.

Degree of separation can be defined in terms of product purities or in terms of component recoveries. The greater the degree of separation, the greater will be the recovery of the light component in the distillate and the heavy component in the bottoms. This will result in higher product purities.

Degree of difficulty of separation is defined as the relative difficulty encountered in separating the two compounds in question, regardless of the purity requirements set by the process specifications. In light ends terminology, it may be considered as inversely proportional to the relative volatility between the two components.

From one's past experience, the following become obvious.

1. For a given system, the tray requirements increase markedly as purity requirements become greater, but reflux requirements increase only a small amount once a relatively high purity level is reached.
2. For a fixed separation, tray and reflux requirements increase as the relative volatility decreases, i.e., the separation becomes more difficult. For example, the propane and n-butane separation is easier than propane-propylene but more difficult than propane and n-pentane.

Speaking qualitatively, at reflux conditions exceeding minimum requirements, tray requirements are directly proportional to the required degree of separation and to the degree of difficulty of separation inherent in the physical-chemical system under consideration. Conversely, for a fixed number of trays, reflux requirements are directly proportional to the degree of difficulty inherent in the system and, to a somewhat lesser extent, to the required degree of separation.

The above terminology is the author's own. However, it is straightforward and, when applied to any distillation system involving discrete components, will result in a rapid qualitative assessment of tray-reflux requirements.

In the refinery, two terms are used to discuss product composition and the degree of separation between adjacent fractions. *ASTM boiling range* defines the general composition of the fraction and is usually one of the key specifications for most distillates from both the atmospheric tower and the vacuum tower.

The second term, *(5-95) Gap*, defines the relative degree of separation between adjacent fractions. It is determined by subtracting the 95 volume percent ASTM temperature of a fraction from the 5 volume percent ASTM temperature of the adjacent heavy fraction.

$$(5\text{-}95)\ \text{Gap} = (t_{5_H} - t_{95_L})_{\text{ASTM}},\ \text{degrees F}$$

Packie's (2) classic paper was the first to disclose criteria for defining fractionation between atmospheric tower distillate streams. Figure 2.6 is Packie's curve for fractionation between the overhead fraction and the adjacent sidestream.

The nomenclature for this correlation is as follows:

1. L_N = gallons per hour reflux from the top tray measured as 60 degree F liquid.
2. D_N = gallons per hour total distillates (vapor and liquid) to top tray, measured as 60 degree F liquid.
3. N_T = number of actual trays in the section, i.e., trays M through N inclusive = $N - (M - 1) = N - M + 1$. Note that each tray in pumparound heat removal service counts as one-third of an actual tray.

Figure 2.7 is Packie's curve for fractionation between sidestream products. The nomenclature for this correlation is as follows:

1. L_M = gallons per hour reflux from the upper draw tray measured as 60 degree F liquid.
2. P_N = gallons per hour total product vapors, measured as 60 degree F liquids, to the upper draw tray, i.e., stream D_N plus all lighter products.
3. N_T = number of actual trays in the section, i.e., M through (N – 1) inclusive = N – M. Note that each tray in pumparound heat-removal service counts as one-third of an actual tray.
4. $\Delta t(50\%)$ = (ASTM 50 percent temperature of the lower sidestream product, D_M) – (ASTM 50 percent temperature of the total products lighter than D_M).

Figure 2.7 does not apply to fractionation between the lowest sidestream and the bottoms stream, nor does it apply to vacuum fractionation although it is often used for the latter purpose due to lack of anything better. Note that these curves apply only for the case where steam stripping of sidestreams is practiced at rates of at least 0.2 pounds steam per gallon of product (8.4 pounds steam per barrel product). Reboiling of sidestreams will also satisfy this stipulation as long as the portion of the sidestream vaporized back is at least equal to that which would be produced by the above-mentioned steam rate. In cases where this

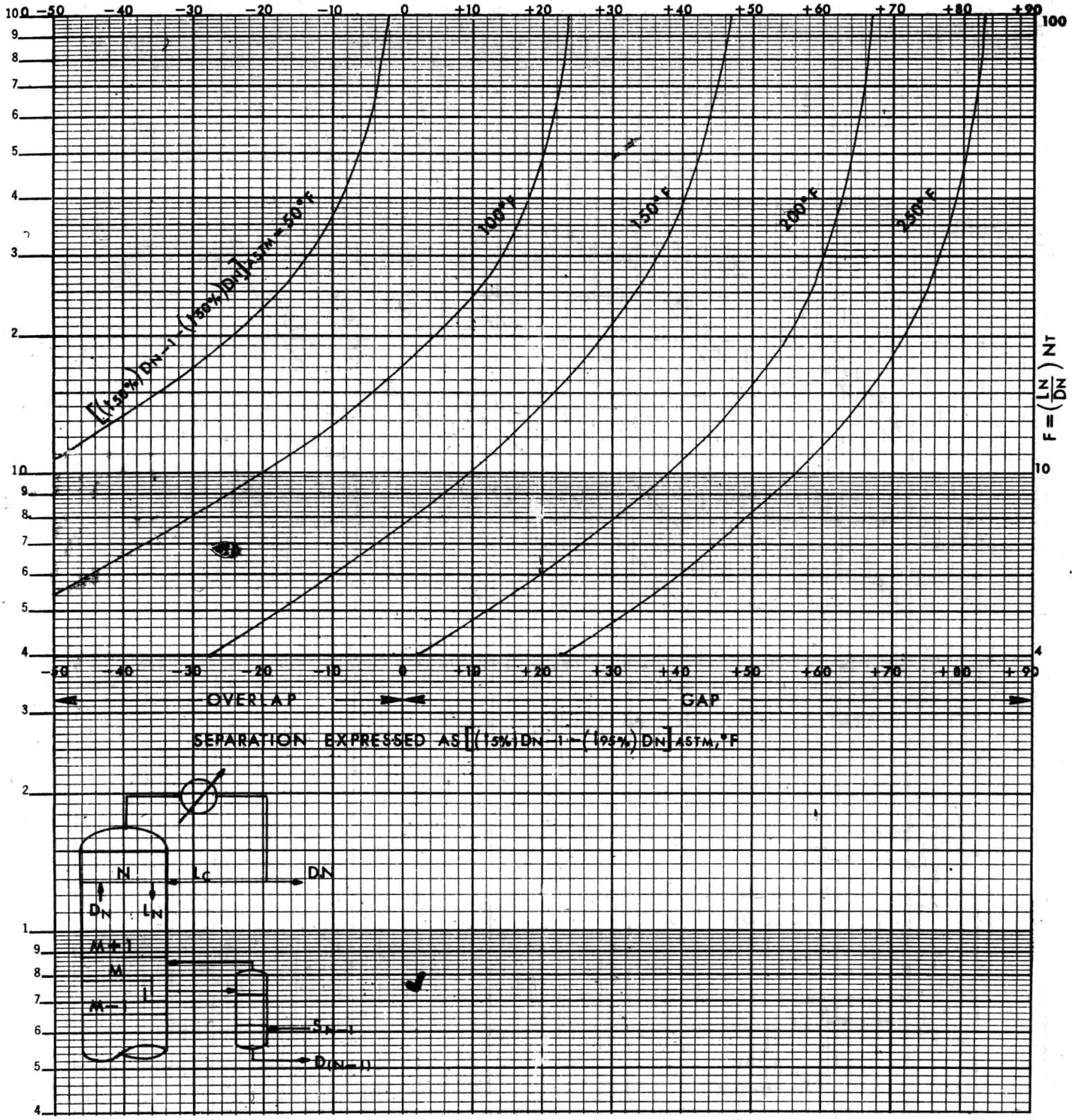

Figure 2.6. Fractionation between total overhead and highest sidestream product, atmospheric crude towers (used with permission of the American Institute of Chemical Engineers).