

July 21, 1931.

W. A. PETERS, JR

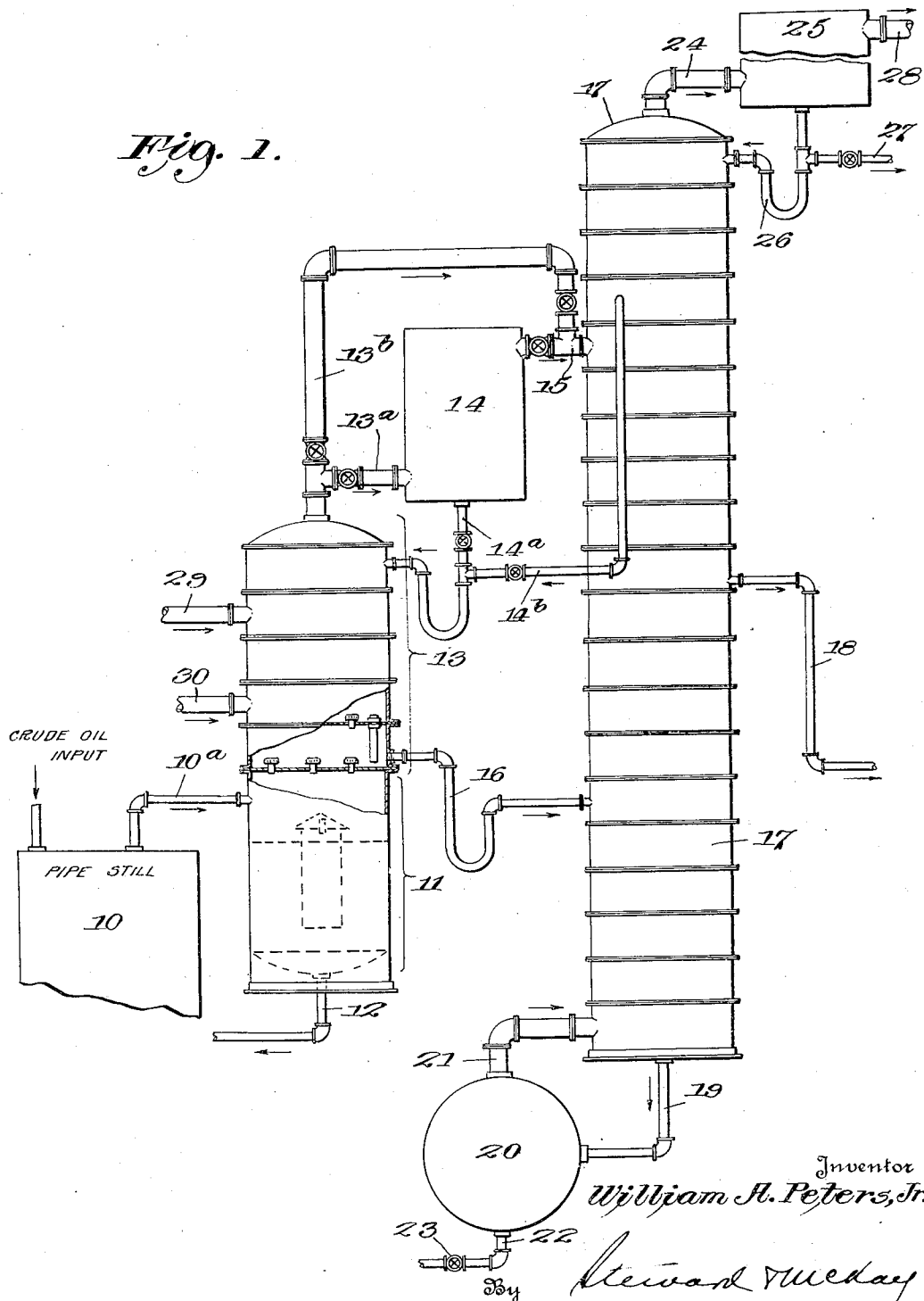
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DISTILLATION OF MINERAL OILS

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Fig. 1.



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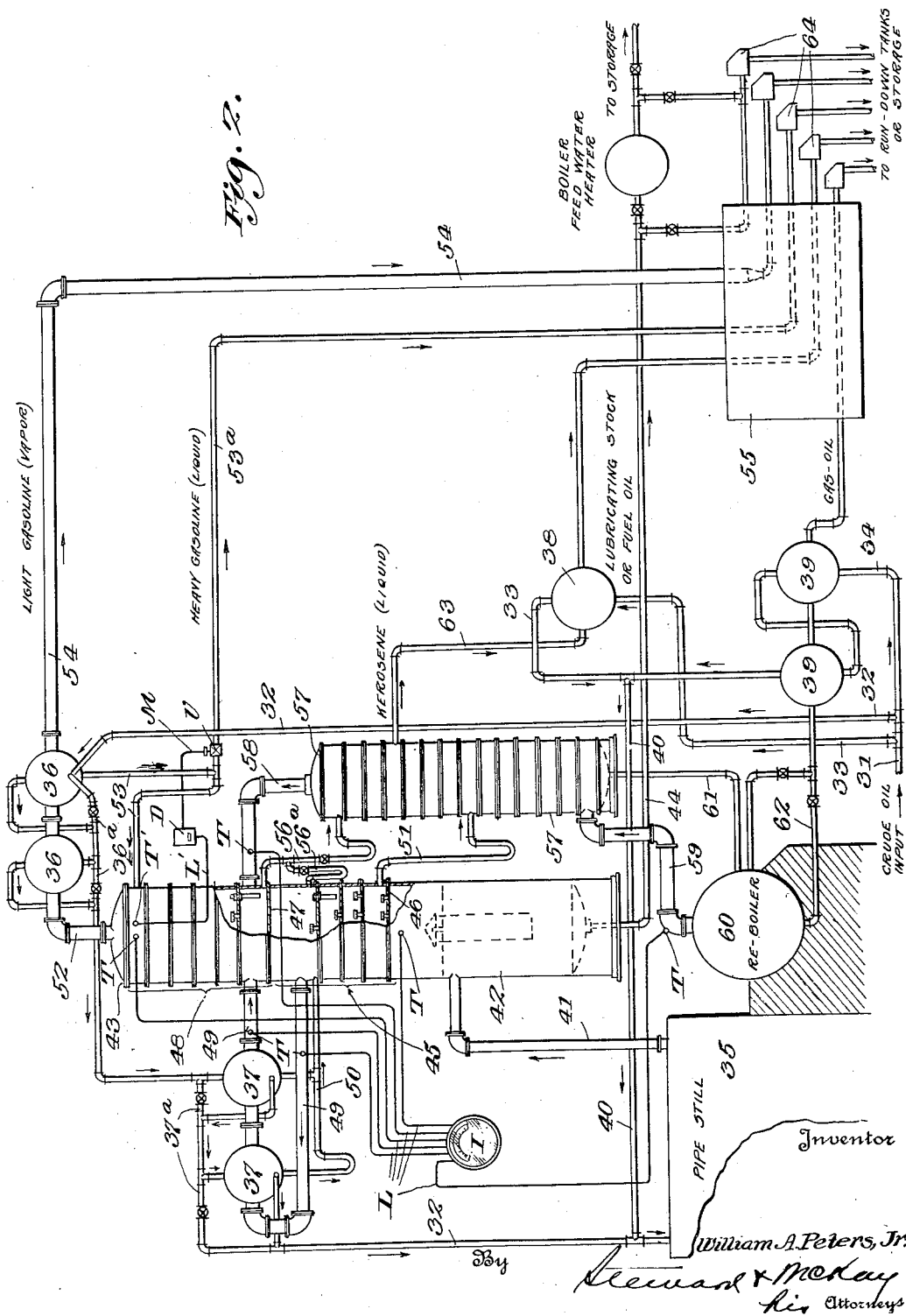
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UNITED STATES PATENT OFFICE

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DISTILLATION OF MINERAL OILS

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This invention relates to distillation of mineral oils; and it has to do more particularly with reduction of crude petroleum to marketable products by a method of fractional distillation enabling the manufacture of sharply cut products in a more efficient manner than has heretofore been employed.

In reducing crude petroleum to marketable products, it has been the custom heretofore to separate certain products more or less roughly by fractional distillation and partial condensation, thus obtaining preliminary crude cuts which are then re-run to give the final cuts desired. Recently it has been found possible by using various types of countercurrent fractionating towers to more nearly approximate the desired final products in one distillation. The final products sought are mixtures of hydrocarbons, and in the trade they are not strictly definite mixtures but may ordinarily vary within rather wide permissible limits, so that methods which allow some overlap in the separation of these several products are often considered satisfactory. Thus, for example, in the manufacture of gasoline, kerosene and gas oil from a normal crude in a one-step distillation process that has recently become available, the results obtained have been considered satisfactory although the kerosene may contain as much as 5 per cent of rather low-boiling material which might better be included in the gasoline cut. Under some circumstances, however, sharper separation than has heretofore been practicable in a one step distillation is desired.

Accordingly, a principal object of the present invention is to render commercially feasible the distillation from mineral oil, directly and without redistillation, of three groups of products separated from each other with the greatest accuracy or sharpness consistent with simple design and economical operation. These three groups may be designated generally as follows: first, a low-boiling portion comprising the gasolines; second, a relatively high-boiling portion comprising chiefly gas oil; and third, a portion comprising products whose boiling points are intermediate the first two groups mentioned and

consisting mainly of the kerosenes, but including also in some cases certain products lighter than and not strictly classifiable as a kerosene but of too high an initial boiling point to be termed properly a gasoline. In particular it is a specific object of the invention to get a relatively sharp cut between the kerosenes (of which one or more may be produced) and the gasolines.

In commercial practice the three groups of products above mentioned are commonly identified approximately as follows: Gas oil is usually considered as a product with an initial boiling point by Engler distillation of about 530° F. and an end point about 700° F. A good kerosene from the standpoint of close fractionation would have an initial boiling point of about 400° F. and an end point of about 520° F. Gasoline is made in several grades with an initial boiling point around 100° F. and end points up to about 450° F. Where two gasolines are made in a given distillation process, one light and the other heavy, it is obvious that it is not feasible to make a clean cut separation between the two, since otherwise the heavy gasoline will be free of light ends and will not be salable.

Generally described, the process of the invention comprises heating crude oil or other mineral oil to a temperature sufficiently high to vaporize the three groups of products before mentioned, namely, gasolines, gas oil, and products intermediate these. The vapors of these products are then subjected to a preliminary fractionation in apparatus of any suitable type in order to obtain, on the one hand, vapors consisting mainly of constituents boiling lower than kerosene and containing very little constituents, if any, boiling higher than kerosene; and, on the other hand, a liquid consisting largely of gas oil, and in any event consisting mainly of constituents boiling higher than kerosene, but also containing a variable minor percentage of constituents belonging properly in the final gasoline and kerosene cuts which it is desired to obtain. The vapors and liquid thus separated as the result of the preliminary fractionation are not in equilibrium relation to each other, but on the contrary are separated by a distinct gap

not characterizing the relation of a liquid and its equilibrium vapor.

The vapors and liquid resulting from the aforesaid preliminary fractionation are now introduced, respectively, into a secondary counterflow rectifying column at different levels therein, the selection of these levels being most desirably such that each of the so-introduced products is approximately in equilibrium with the liquid and vapor present in the column at the level where that product is introduced. This is an optimum condition, however, and not an absolutely rigid requirement of the process. By properly controlling the reflux to the secondary column, it is possible under these conditions of operation to withdraw a kerosene from a point or points in said secondary column intermediate the levels at which the preliminarily separated vapors and liquid are respectively introduced thereinto.

By way of further explanation of the principles underlying the invention, an example illustrating a practical way in which the invention may be applied to the distillation of a typical crude oil will now be given, reference being made to the accompanying drawings which illustrate apparatus systems suitable to use in carrying out the new process. In these drawings, which are to be understood as more or less diagrammatic in character, Fig. 1 illustrates one such system of apparatus in side elevation, while Fig. 2 represents an arrangement somewhat different structurally but similar in operating principle.

It will be assumed in the following specific example that the mineral oil to be distilled is a crude of 38° Bé. gravity and yielding upon test distillation by the Engler method about 32 per cent gasoline, 6 per cent kerosene, and 25 per cent gas-oil, the remaining 37 per cent being residue and loss. The crude oil is first brought to a temperature sufficiently high to insure vaporization of the desired constituents thereof at substantially ordinary atmospheric pressure. This may be accomplished in various ways, but in using the system illustrated in Fig. 1, which will be first considered, the oil is heated up in pipe still 10 through the coils of which it is forced under substantial pump pressure and in which it attains a temperature approximating 625° to 650° F. The crude oil thus superheated under pressure in the pipe still is discharged through pipe 10^a into a vaporizer 11 of any appropriate character wherein the pressure is practically atmospheric or so slightly thereabove as may be necessary to overcome the frictional resistance to passage of vapors through the apparatus system. Vapors of the desired constituents of the crude are flashed off in the vaporizer and separated from the unvaporized constituents constituting the liquid

residue, which residue may be worked up as lubricating stock or sold as fuel oil depending upon the character of the particular crude undergoing treatment. This liquid residue may be led away from the vaporizer through outlet pipe 12.

The vapors separated in the vaporizer are then subjected to a preliminary fractionation in countercurrent fractionating apparatus to obtain a liquid product and a vapor product, the vapors consisting mainly of constituents lighter than kerosene, and the liquid product consisting mainly of constituents heavier than kerosene. In the system illustrated in Fig. 1, the countercurrent fractionating apparatus comprises a rectifying column or tower 13 surmounting the vaporizer 11 and into which the separated vapors pass directly from said vaporizer. This rectifying tower or column may be of any suitable type, but in the present example it is of the bubbler-cap type well known to those skilled in the art and therefore requires no detailed description here. Vapors leave the top of this column by way of outlet pipe 13^a at a temperature approximating 450° F., for example, pass into and through a partial condenser 14, where the higher boiling portion thereof is condensed to provide reflux which returns to the top of the column through trapped line 14^a. Condenser 14 may be omitted and the necessary reflux obtained by withdrawing a liquid of approximately similar composition to that which would be obtained from condenser 14, from an appropriate plate of column 17. In that case vapors go through line 13^b direct to column 17, while reflux liquid is returned through line 14^b. The uncondensed vapors pass off through pipe 15. The liquid product resulting from this preliminary fractionation is conducted from the lowest plate of column 13 through trapped line 16.

The operation of the preliminary fractionating column 13 should be so regulated and controlled that the overhead or vapor product leaving through pipe 15 contains substantially no material boiling above a predetermined temperature, say 500° F. in the present example. The liquid product leaving the lowest plate of said column 13 is in approximate equilibrium with the vapors passing upwardly through said lowest plate from the vaporizer below and may contain 30 per cent of material boiling below the boiling point of the highest boiling material leaving the top of column 13 as vapor. There is therefore a certain overlapping in boiling range of the vapor and liquid products obtained from the preliminary fractionating column 13. If it be desired to reduce the amount of this overlapping, as may be desirable under some circumstances this can be accomplished by a slightly modified

procedure which will be explained hereinafter.

The aforesaid vapor from the top and the liquid from the bottom of preliminary fractionating column 13 are now further treated in countercurrent fractionating apparatus in order to produce the desired sharply cut final product. To this end said vapor and liquid are introduced into a secondary fractionating column indicated generally at 17, at substantially different levels. In the upper part of this secondary fractionating column, the material contained in the vapors entering through pipe 15 and boiling above the desired end point of the gasoline that is to be made, is removed from the vapors by countercurrent scrubbing and flows downwardly through said tower or column. On the other hand, the light material boiling below 500° F., which is contained in the liquid entering through pipe 16, is vaporized and passes upwardly through said tower. Such gasoline constituents as are present in this vapor pass for the most part to the top of the column without being liquefied, while most of the constituents of said vapor boiling below 500° F. but above the desired end point of the gasoline collect as liquid on a plate or plates in column 17 intermediate the points at which pipes 15 and 16 enter said column, together with the products boiling between 450° and 500° F. that were contained in the vapors entering said column through pipe 15. Therefore one or more sharply cut products, intermediate a gasoline on the one hand and gas-oil on the other, and containing but a small proportion of the already small proportion of light material in the vapor coming from the lower part of the column, can be withdrawn as a liquid from the secondary fractionating tower or column. Such an intermediate product, assumed in this instance to be a kerosene is withdrawn in liquid form through pipe 18 from an intermediate point in the column as shown, most desirably about midway between inlets 15 and 16.

It will be noted that the end point of the material leaving the primary column 13 as vapor can be very definitely controlled, whereas the initial boiling point of the liquid material leaving the bottom of the primary column can not be controlled to a similar extent as a practical matter, said liquid material being mostly gas oil but containing constituents boiling all the way down into the gasoline range. But since substantially all the gasoline constituents at points in the secondary column 17, above the point at which this liquid product of the preliminary fractionation is introduced, will be in vapor form as already pointed out, a kerosene cut practically free of gasoline may be drawn off in liquid form.

The liquid coming from the base of the

primary column 13 through pipe 16 may be assumed to be at a temperature approximating 500° to 525° F. In order to remove the kerosene and even all the gasoline from this liquid by ordinary distillation methods, it would be necessary to raise the temperature of the liquid to about 620° F. which, of course, would cause more or less heavy material to boil off in addition to the lighter products sought. According to the present method, however, this heavier material is separated by countercurrent scrubbing and made to pass downwardly in a manner similar to that by which the heavier material is cut out of the vapors in the upper part of column 17.

The liquid oil leaving the bottom of column 17 passes through pipe 19 to a re-boiler 20 and vapors from this re-boiler, at a temperature of say 650° F. or thereabouts, are conducted into the base of said column through vapor pipe 21, thus supplying to said column the necessary heat in addition to that entering at 15 and 16, to maintain the proper operation of the column. By reason of the preliminary fractionation effected in column 13, the re-boiler 20 is required to handle very much less material than would otherwise be necessary and hence a substantial saving in operation and equipment is made possible. Stripped gas-oil is discharged from the re-boiler through pipe 22 having a control valve 23, the effective opening of which may be regulated in such manner as to maintain a constant level of liquid in the re-boiler.

The light vapors leaving the top of column 17 through vapor line 24 pass to a condenser 25, and a part of the resultant condensate is refluxed through trapped line 26 back to the column 17 to maintain the proper countercurrent fractionating conditions therein. The excess of gasoline condensate passes to storage through valved line 27, while any vapors and gases escaping condensation in 25 pass off through vapor line 28.

The approximate figures hereinabove given for temperatures and characteristics of products are of course subject to wide variation.

It is again desired to emphasize the importance of the preliminary step of first partially fractionating the crude oil vapors in order to obtain two cuts which with respect to their properties straddle, so to speak, the product or products which it is desired to take out as one or more intermediate cuts between the heaviest and the lightest products to be made, namely, gas-oil and gasoline. To enable applying this principle of operation with even greater certainty and effectiveness, the procedure described in the specific example hereinabove given may be modified by vaporizing the desired constituents of the original crude oil continuously in a plurality of successive stages and introducing into the primary column 13 the vapor

products of said stages simultaneously at separated points in said column. For example, assuming that the desired constituents of the crude are vaporized in two stages, the first stage vapors or lighter portion may be introduced through pipe 29 into the upper part of column 13, while the heavier portions are introduced through pipe 30 into a lower section, the points of introduction being most desirably so selected that in each instance the introduced vapors are in approximate equilibrium with the vapors and liquid present in that section of the column. By such an expedient the overlap in boiling range between the vapor product and the liquid product obtained in the preliminary fractionation treatment in column 13 may be reduced to say 10 per cent or thereabouts. For example, where the crude is preheated in heat exchangers to a temperature of say 450° F., the oil thus preheated may be allowed to flash off light vapors, chiefly gasoline constituents, which may then be introduced through pipe 29 into the upper part of column 13; the residual oil being then further heated to say 625° F. or thereabouts to vaporize the remaining heavier desired constituents which may be introduced into the column through pipe 30. If desired, the vapors introduced through inlets 29 and 30 may be derived from pipe-still and vaporizer units like the unit 10—11 here illustrated, or of any other appropriate type, and these may operate successively upon the oil in conjunction with said unit 10—11, the combination thus supplying vapors from three distillation stages simultaneously to column 13. Or any other suitable means may be employed to supply vapors of the desired crude oil constituents either in one stage or several successive stages.

As a rule the preliminary fractionator 13 need comprise only about four to six bubbler-cap sections, or the equivalent of this in other types of countercurrent fractionating apparatus to enable accomplishing satisfactorily the preliminary fractionation characterizing the present process; but this is not to be understood as restrictive. In the present example, fractionator 13 comprises five bubbler-cap sections.

In using the system illustrated in Fig. 2 to carry out the new process, the procedure is similar in principle to that already described. The arrangement of the apparatus is in some respects more convenient, however, and permits of substantial economies in design and operation. The crude oil to be distilled, which for the sake of an example may be assumed to be of 38° Bé. gravity before mentioned enters the system under pump pressure through line 31 and may then pass by way of any or all of lines 32, 33 and 34 to suitable still means which in this instance is a pipe still indicated conventionally at 35. In line 32 are interposed sets of heat

exchangers 36, 37, in which the incoming crude may absorb heat from the hot vapors present in parts of the system to be mentioned presently. In line 33 is arranged a heat exchanger 38 by which the crude may absorb heat from an intermediate liquid distillate such as kerosene, resulting from the distillation; while in line 34 are heat exchangers 39 wherein gas-oil resulting from the distillation may give up heat to the incoming crude. Lines 33 and 34 both conduct crude to line 40 which joins line 32 near the point of entrance into the pipe still 35, as indicated. valved by-passes may be provided for cutting out any of the heat exchangers when desired. Such by-passes are indicated, for example, at 36^a and 37^a in connection with heat exchangers 36 and 37.

The crude oil, coming from line 32 or line 40, or both, is pumped through the coils of the pipe still 35, and heated to a temperature of say 625° to 650° F. The oil is forced through the pipe still under considerable pressure, as much as 200 pounds per square inch in some cases, supplemental pump means (not shown) being provided wherever necessary to insure adequate and continuous feed of the oil through the pipe still. The superheated oil, together with such vapors as are formed in the passage through the pipe still, are discharged through line 41 into vaporizer chamber 42, corresponding in function to vaporizer 11 of the apparatus shown in Fig. 1. Said vaporizer chamber 42 comprises the lower part of a tower or column indicated generally at 43. The pressure in said vaporizer chamber is approximately atmospheric, and upon discharge of the superheated crude oil thereinto through pipe 41, vapors of the constituents desired to be recovered therefrom are flashed off and pass upwardly, while the heavier unvaporized portions of the crude flow downwardly and leave the bottom of the column through residuum discharge line 44, the contained heat units being utilized, if desired, to pre-heat crude or boiler feed water, for example.

The flashed-off vapors, of which the temperature may approximate 525° F. in a typical instance, pass upwardly from the vaporizer chamber into a preliminary fractionating portion 45 of the tower, said section being included between plates 46 and 47 in said column. In this instance also the column is assumed to be of the bubbler-cap type, although it may be of any type suitable to effect countercurrent fractionation. Plate 46 is provided with the usual up-tubes and bubbler-caps for upward passage of vapors from the vaporizer 42, but does not have a liquid down-pipe, and liquid collecting on this plate does not flow down into the vaporizer. Plate 47 is a blank plate entirely separating the portion 45 of the column from the remaining upper portion 48 which will

be referred to again presently. In a typical instance, portion 45 of the column, which corresponds in function to preliminary fractionator 13 of Fig. 1, may comprise from 4 to 6 bubbler-cap sections. Through this preliminary fractionator 45 the vapors travel upwardly in countercurrent contact with downwardly flowing liquid, the persisting vapors passing off through vapor line 49. The temperature of these vapors when they leave the preliminary fractionator 45 may approximate 450° F. in a typical instance. These vapors are passed through heat exchangers 37 wherein they give up heat to incoming crude and are cooled to say 400° F. They consist mainly of constituents that are lower boiling than kerosene and contain substantially no constituents boiling above 500° F. The condensate resulting from the cooling in heat exchangers 37, is refluxed through line 50 into the top of the preliminary fractionator 45. Liquid descending to plate 46 is discharged from the column through trapped line 51. This liquid consists principally of constituents boiling higher than kerosene but also contains lower boiling constituents, including some that belong in the gasoline cut. In other words, the vapor and liquid products made in the preliminary fractionator 45 are similar to those made in preliminary fractionator 13 of the apparatus shown in Fig. 1.

The vapors leaving preliminary fractionator 45 are now further fractionated to eliminate heavy ends, while the liquid product leaving said preliminary fractionator is fractionated to eliminate gasoline and most of the kerosene it contains, all in such manner as to enable the production of a sharply cut intermediate product which in this instance may be assumed to be a kerosene. The vapors leaving heat exchangers 37 through line 49 enter the base of upper portion 48 of the tower or column just above plate 47 and pass upwardly through the bubbler-cap sections thereof against downwardly flowing liquid refluxed to the top of the tower. In typically satisfactory practice, the amount of such reflux is so controlled that vapors leaving the top of the column through vapor line 52 are at about 350° F. They pass thence through heat exchangers 36 where they are cooled enough to provide condensate, in the form of a heavy gasoline, sufficient in quantity to supply the necessary reflux to the top of the column through reflux line 53, residual vapors of light gasoline going on through line 54 to condenser coils (not shown) included in a condensing and cooling system indicated diagrammatically at 55, where a resultant light gasoline condensate is obtained. Any excess of heavy gasoline condensate beyond what is needed as reflux passes to the cooling system through line 53^a in which is located a control valve V.

Liquid descending to blank plate 47 at the bottom of the upper portion 48 of the column leaves the column through trapped line 56 and is introduced into the top of a second column indicated generally at 57 which may be of smaller diameter than column 43 but which virtually functions, in conjunction with portion 48 of column 43, as one column, or a column combination, corresponding to column 17 of Fig. 1. It will be noted in this connection that vapors pass from the top of column 57 through vapor line 58 into the lowermost section of portion 48 of column 43; and the operation of column 57 is so controlled that the temperature of the vapors thus entering column 43 through line 58 is substantially the same as that of the vapors entering through line 49.

Liquid leaving the preliminary fractionator 45 through line 51 is introduced into column 57 a number of sections below the top. This liquid enters at a temperature of say 500° F. or thereabouts in a typical instance, and in passing down through the sections of the fractionating column 57 is stripped of practically all of its gasoline and kerosene content by countercurrent contacting with ascending hot vapors supplied at, say, 625° to 650° F. to the base of the column through vapor pipe 59 from a re-boiler 60 into which liquid flows from the bottom of the tower through pipe 61. Stripped gas oil flows from the re-boiler to cooler 55 through line 62 in which the heat exchangers 39 are located.

If desired, vapors may be passed directly from portion 45 of the tower or column 43 to portion 48 of said column, heat exchangers 37 being omitted in this case, and suitable reflux liquid being withdrawn from pipe 56 and supplied through pipe 56^a to the top of portion 45 of column 43. Under these conditions, the operation would therefore be analogous to the alternative procedure described in connection with Fig. 1 where, as was pointed out, the vapors might pass directly from column 13, through line 13^b, into the upper part of column 17.

At one or more points in column 57, above where liquid is fed in through pipe 51, one or more intermediate products may be drawn off as in the procedure previously described in connection with Fig. 1. In the present instance a single kerosene product is assumed to be drawn off in liquid form through pipe 63, passing through heat exchanger 38 and thence to 55 for final cooling. It will be noted that the section of column-combination 57, 48 from which the liquid kerosene is withdrawn is substantially equidistant from the sections into which the vapor and liquid products from the preliminary fractionator 45 are respectively introduced through pipes 49, 51. While the location of the kerosene draw-off may be varied within reasonable limits, it will usually be found that most satisfactory

results are obtainable under these conditions.

Means should be provided for accurately observing the temperature in various parts of the apparatus in order to enable close control of operating conditions. To this end a system of pyrometers is most desirably provided, having thermo-couples located at points 'T' in the various vapor spaces and vapor lines where observation and control of the vapor temperature is essential or desirable. Leads L connect the several thermo-couples T to a conveniently located indicator I where the temperatures may be observed.

As accurate control and regulation of the amount of reflux to the top of the main column 42 is desirable at all times, provision may be made for automatically controlling the amount of such reflux by the temperature of the vapors leaving the top of the column. In this instance the thermo-couple T' located adjacent the vapor outlet 52 is connected by lead L' to an electrical control device indicated generally at D which operates through appropriate actuating mechanism M to control valve V, whereby the valve may be opened or closed according as it may be necessary to decrease or increase the amount of reflux to the top of the column to maintain the desired operating conditions.

The various products made in the distillation may go from the condensing or cooling system to run-down tanks or storage, as indicated, look boxes 64 being placed in the run-down lines as desired.

It is to be understood that the invention in its broader aspects is not restricted to the details of operation given above, and that the specific embodiments of the process described in explaining the underlying principles involved are merely illustrative and not intended to be limiting.

What is claimed is:

1. The process of distilling mineral oil for production therefrom of a gasoline fraction, a gas-oil fraction, and an intermediate fraction, which comprises heating mineral oil in continuously successive stages to provide a corresponding plurality of vapor products of successively higher boiling points, introducing said plurality of vapor products simultaneously into a preliminary countercurrent fractionating column at different levels corresponding generally to the points at which the vapor products so introduced will be most nearly in equilibrium, respectively, with the vapors and liquid in said column, conducting from the upper part of said column a resultant vapor fraction consisting mainly of constituents lower-boiling than kerosene and passing the same into the upper part of a second countercurrent fractionating column, conducting from the lower part of said preliminary fractionating column a liquid consisting mainly of constituents higher-boiling than kerosene and introducing the same into

said second column at a point substantially below that at which the vapor fraction was introduced, condensing and refluxing to the upper part of said second column a part of the vapor products issuing therefrom, and withdrawing from a point in said second column, intermediate the points at which the aforesaid vapor and liquid fractions were introduced, a liquid product of boiling range intermediate the boiling ranges of gasoline and gas-oil.

2. The process of distilling mineral oil as defined in claim 1, further characterized by the fact that the vapor and liquid fractions preliminarily separated in the first column are introduced into the second column at points corresponding generally to those at which they will be, respectively, most nearly in equilibrium with the vapors and liquid in said second column.

In testimony whereof I hereunto affix my signature.

WILLIAM A. PETERS, JR.