

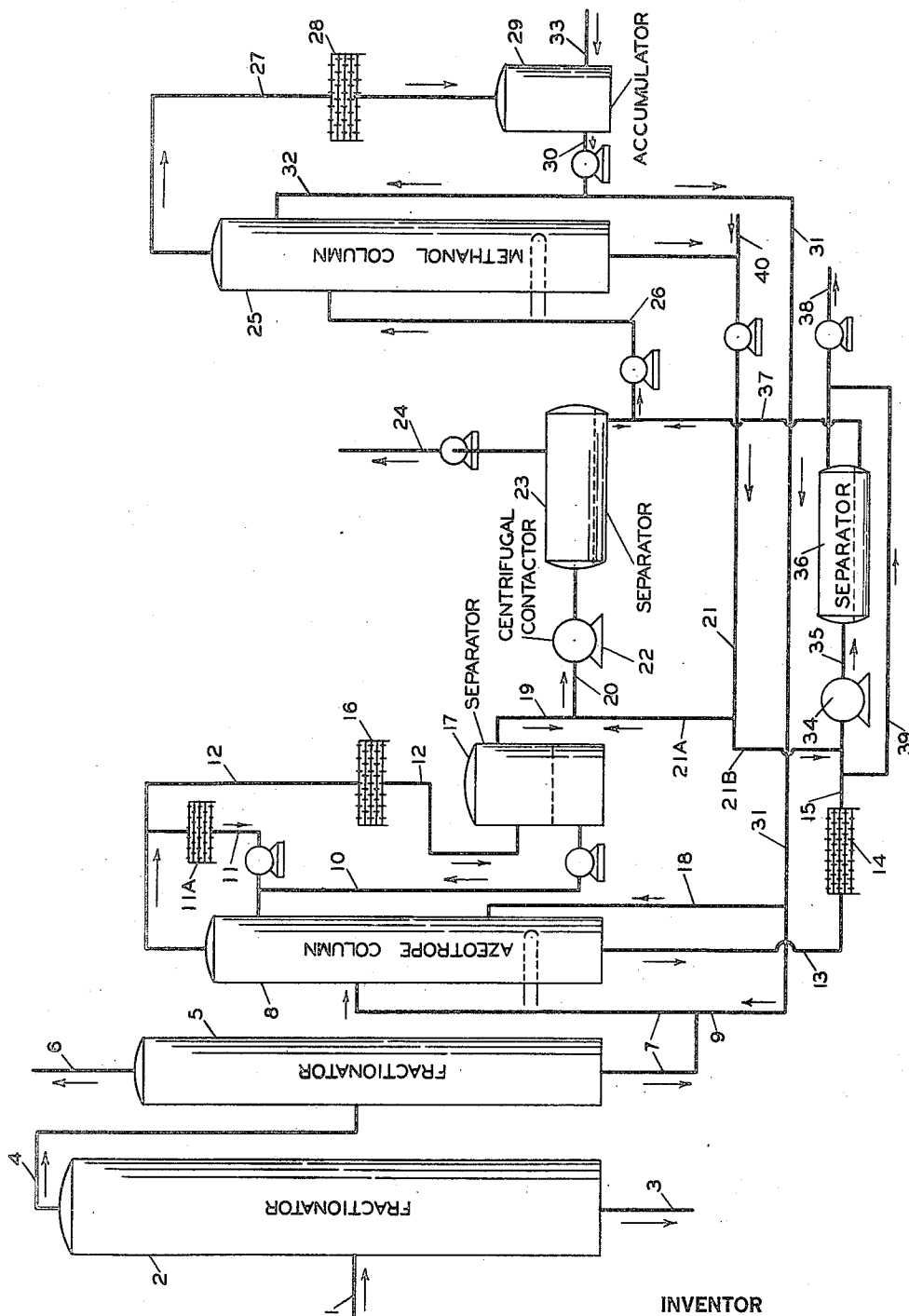
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SEPARATION OF HYDROCARBONS

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SEPARATION OF HYDROCARBONS

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This invention relates to the separation of complex hydrocarbon mixtures and particularly to the segregation of a high-octane-number naphthenic hydrocarbon from admixture with a low-octane-number paraffinic hydrocarbon, namely methyl cyclopentane from normal hexane.

In the blending of hydrocarbons to produce aviation fuels, the hydrocarbons to be used must be chosen with regard to their anti-detonating qualities, response to anti-detonants such as tetraethyl lead, volatility, storage stability, etc. In order to produce aviation fuels to meet the ever increasing standards required by modern aircraft, especially those used for military purposes, the use of naturally occurring or synthetically produced complex hydrocarbon mixtures is gradually being replaced by careful segregation steps designed to eliminate specific hydrocarbons of undesired characteristics and/or to obtain specific hydrocarbons having one or more of the qualities desired in any particular fuel blend.

It is known that naphthenic hydrocarbons have good octane numbers, that isoparaffins have octane numbers ranging from poor to very good depending upon the complexity of structure, and that normal paraffins have very poor octane numbers. Generally, the isoparaffins present in naturally occurring complex hydrocarbon mixtures are not those of the highest octane number. Accordingly, various efforts have been made to obtain some sort of segregation of naphthenes from paraffins so as to obtain improved blending stocks. However, so far as I know such processes have only succeeded in attaining an imperfect separation into mixed naphthenes containing more or less residual paraffins, or expensive and inefficient batch-type operations have been resorted to without accomplishing the substantially complete separation which is so desirable.

It is recognized that the octane number or anti-detonating quality of a fuel is dependent upon the operating conditions of a motor using the same, and may vary considerably with such factors as load and the air-fuel ratio. In ordinary usage, an internal combustion engine is operated under conditions approaching maximum economy, the most important of these conditions being the use of a high air-fuel ratio, or "lean mixture." However, in military planes, especially those used for interceptor and pursuit service, a low air-fuel ratio, or "rich mixture," must frequently be used during periods of great acceleration such as taking-off and climbing, and economy of operation is of secondary importance. Production of maximum possible power during

such periods is of prime importance. It has been discovered that aviation fuels consisting essentially of highly branched paraffins, for example iso-octane or neohexane, do not operate in a completely satisfactory manner when it is necessary to use a rich mixture, the power production not being so great as desired and the tendency toward detonation sometimes increasing. On the other hand, it has recently been found that certain naphthenes are especially desirable components in high-octane aviation gasolines used for fast fighting planes, due to the fact that their anti-detonating qualities and the power produced by them, when a rich mixture is used, are relatively much superior to the same properties exhibited by highly branched paraffins. Since these naphthenes in lean-mixture operation do not have such a high knock rating as the highly branched paraffins, an aviation fuel to be used in combat service is preferably made up of a blend of such paraffins with substantial proportions of the most desirable volatile naphthene or naphthenes, for example cyclopentane and methyl cyclopentane, to produce a finished fuel of balanced properties under all conditions of actual motor operation. Such fuels may advantageously contain up to one-third or more naphthene.

Accordingly, it is now of exceedingly great importance to find a practical and commercially feasible process for preparing substantially pure single naphthenes. Accomplishment of such a result will enable one to prepare more readily an aviation fuel of optimum properties for any given conditions of operation.

It should be pointed out, furthermore, that various other hydrocarbons, such as n-hexane, even though not suitable for use in aviation fuels because of their low octane number or other undesirable properties, may, if obtainable in substantially pure form, find different uses which make the pure compound much more valuable than an ordinary impure commercial fraction.

Methyl cyclopentane is a valuable naphthene which occurs naturally in relatively small amounts in such complex hydrocarbon mixtures as natural and straight-run gasoline. The complexity of the mixture requires very efficient fractionation to accomplish even a partial segregation, but a final product of high purity cannot be obtained by this means alone, due to the apparent formation of a constant-boiling mixture of methyl cyclopentane with n-hexane. I have now devised a process utilizing azeotropic distillation with methanol under certain conditions, which enables me to isolate methyl cyclopentane and n-hexane

one from the other, each substantially pure, if desired, in an economical and practical manner, as will be more fully disclosed hereinafter.

Not only is it important that methyl cyclopentane be obtained substantially free from n-hexane, but it is also of importance to recover as much of the methyl cyclopentane as possible due to its relative scarcity. Thus, controlling conditions so that the n-hexane produced is relatively free from residual methyl cyclopentane is an important aspect of my invention. Furthermore, pure n-hexane may be needed for various purposes so that the n-hexane produced by the utilization of my invention frequently has considerable economic value over and above the ordinary impure fractions obtainable by simple fractionation of petroleum.

The difficulties involved in obtaining a really efficient separation will be realized by a consideration of the boiling points of the two hydrocarbons in question. At standard atmospheric pressure, n-hexane boils at 155.8° F. (68.8° C.) and methyl cyclopentane boils at 161.2° F. (71.8° C.) However, as stated above, the separation is much more difficult than would be anticipated even with these close boiling points, inasmuch as apparently a constant-boiling mixture is formed between the two hydrocarbons. This will be readily seen in Example 1 below.

It is an object of this invention to provide for the separation of a complex hydrocarbon mixture into one or more substantially pure components.

Another object is to provide a batch or continuous process for recovering methyl cyclopentane from admixture with other hydrocarbons, especially n-hexane.

Still another object is to provide a continuous process in which an essentially two-component mixture of n-hexane and methyl cyclopentane is fractionated out from a more complex mixture of hydrocarbons and then subjected to azeotropic distillation under certain specific conditions in the presence of methanol in order to obtain a complete separation with the consequent recovery of substantially pure methyl cyclopentane, which may or may not be admixed with methanol, on the one hand, and substantially pure n-hexane admixed with methanol on the other hand.

Another object is to provide a continuous process for such separation, further characterized by steps accomplishing the efficient separation of methanol from the hydrocarbon products.

Various other objects, as well as advantages, of my invention will become apparent from the following detailed description.

Briefly, one form of my invention contemplates (1) fractionating a complex hydrocarbon mixture containing n-hexane and methyl cyclopentane to obtain an essentially two-component mixture of said n-hexane and methyl cyclopentane, (2) fractionating said two-component mixture with methanol under certain specific conditions hereinafter disclosed in detail so as to remove methyl cyclopentane plus methanol as a bottom product and n-hexane plus methanol as a top product, (3) cooling said top product to form two phases, (4) recycling the methanol-rich phase to the fractionation, preferably as reflux, (5) admixing the n-hexane-rich phase with a small quantity of water and settling to separate an upper n-hexane layer substantially free from methyl cyclopentane, methanol, and water, and a lower methanol-water layer substantially free from hydrocarbons, (6) separating said lower

methanol-water layer into its components which are re-used in the process, and (7) separating substantially pure methyl cyclopentane from the bottom product of the fractionation, preferably by water-washing in a manner similar to that described in steps (5) and (6) above.

Alternately to steps (2) and (7), the proportion of methanol used may under certain conditions be so regulated that substantially pure methyl cyclopentane may be removed as a bottom product ready for immediate use without further treating.

The accompanying drawing is a schematic flow-sheet showing one arrangement of apparatus for carrying out my invention in a continuous manner.

I have found that I may obtain pure n-hexane and pure methyl cyclopentane by treating complex hydrocarbon mixtures containing the same under certain operating conditions which will now be disclosed in detail. The most common sources of the desired material are natural gasoline and straight-run gasoline, which are mixtures of straight-and branched-chain paraffins, naphthenes, and possibly small traces of aromatics. Of course, any other source may be used; however, if hydrocarbon types other than paraffins and naphthenes are in such source, for example olefins, they are preferably first removed by polymerization or like processes, in order to decrease the complexity of the hydrocarbon mixture. Such natural gasoline or similar material is fractionated in an efficient fractionating column or columns in order to separate out hydrocarbons other than n-hexane and the close-boiling naphthene, methyl cyclopentane. In the embodiment shown in the drawing, the hydrocarbons heavier than methyl cyclopentane, i. e., heptanes and heavier, are removed as a bottom product from a first fractionator, while lighter compounds including n-hexane and methyl cyclopentane are taken off overhead. Generally, no isoheptanes are allowed to pass from the top of the column since they would merely complicate the subsequent separation. Accordingly, a very small amount of methyl cyclopentane is lost to the heptanes and heavier cut due to the fact that perfect separation is not attainable under commercial conditions. However, this will only be a small fraction of the methyl cyclopentane present in the charge stock and of course economic factors such as the desired final purity, operating and equipment costs, etc., will determine the sharpness of the cut to be made at this point. If it is preferred to recover all the methyl cyclopentane even at the cost of a slight final contamination or increased difficulty of later separation due to traces of isoheptanes, cyclohexane, or benzene taken overhead, it will be desirable to have the volume of overhead product as small as possible, since under given operating conditions, the percentage of heavier hydrocarbon in the overhead will be about the same, say about one per cent, more or less independently of the total volume of the overhead. Accordingly, the general practice will be to charge a de-pentanized cut to the fractionating column in question. Thus removal of pentanes, and preferably also some of the iso-hexanes, is preferably accomplished previously in separate fractionating means.

The methyl cyclopentane, n-hexane, and lighter overhead product is now taken to another efficient column where all material lighter than n-hexane

is taken off overhead, leaving a n-hexane and methyl cyclopentane mixture as kettle product.

In another way of carrying out the preliminary fractionation, the natural gasoline may be first depentanized, the kettle product from this fractionation de-isohexanized in a second column, and the kettle product from this second column then fractionated in a third column to take off an overhead product comprising essentially n-hexane and methyl cyclopentane. This method of fractionation has been carried out successfully as follows: A pentane-free natural gasoline was fractionated in the second column, which was 12 feet in diameter and contained 70 trays. This column was operated with a reflux ratio of 10.3 to 1, a top temperature varying from 162 to 202° F. with corresponding top pressure of from 10 to 30 pounds per square inch gage, depending upon cooling water temperature, steam pressure, and other factors, and with kettle temperature and pressure varying from 210° F. and 20 pounds to 244° F. and 40 pounds per square inch gage. N-hexane and heavier was produced as a kettle product, which was fractionated in the third column, which was 9½ feet in diameter and contained 40 trays. Using a reflux ratio of 15.7 to 1, top conditions of from 180° F. and 9 pounds to 222° F. and 29 pounds, and kettle conditions of from 250° F. and 15 pounds to 292° F. and 35 pounds per square inch gage, a normal hexane concentrate containing also methyl cyclopentane was produced as the overhead product.

After the mixture of n-hexane and methyl cyclopentane has been partially segregated as described above, it is pumped into a fractionating column into which methanol is also introduced. This column is operated at a pressure above about 10 pounds per square inch gage and preferably not above about 50 pounds per square inch gage, and at a temperature at the top of the column above about 140° F. and preferably not above about 195° F. If substantially pure products are desired, the reflux ratio used, based on the hydrocarbon product taken from the system by removal from the overhead product, is in the range of about 20 to 1. If the reflux ratio is decreased to a value appreciably lower than about 20 to 1, the purity of the product obtained decreases greatly. The ratio may be increased on up to a maximum of say 100 to 1 to obtain the purest possible product, but the rate of increase in purity obtained by increasing the ratio above about 20 to 1 is very small, and frequently it will be found that using a higher reflux ratio is economically unsound. The reflux ratio in this case is defined as the liquid volume of the total reflux (methanol plus hydrocarbon) divided by the liquid volume of the hydrocarbon content of the overhead product which is completely removed from the fractionation system. The liquid volume ratio of n-hexane to methanol entering the column must generally be maintained substantially lower than 2.2 to 1. With reference to this ratio, the methanol referred to is all the methanol entering from any source, whether as fresh feed, reflux, etc., and the n-hexane referred to is all the n-hexane entering from any source, whether as fresh feed to be segregated, or mixed with methanol and returning as a methanol-rich stream or as reflux. When the ratio is thus maintained at less than 2.2 to 1, the kettle product will contain some methanol if the overhead product corresponds to the azeotropic composition. If an overhead richer in methanol than the azeotrope is pro-

duced, the kettle product may or may not contain methanol.

When the above listed conditions are used, the fractionating column need not be of extremely high efficiency; 50 theoretical plates are generally more than sufficient for continuous operation, and the number may be considerably less than 50, particularly in batch operation. However, the column is preferably equivalent to at least 35 theoretical plates. I have found that a substantially complete separation may be accomplished under these conditions, which separation is further illustrated in Example 2 herebelow, and which is in great contrast to results reported by previous workers in the field, who could not even approach the separation of pure components without a large number of fractionations and/or other treatments, even though operating in very efficient stills at atmospheric pressure.

In some circumstances, the ratio of n-hexane to methanol entering the column, as referred to above, may be so controlled that it is equal to the ratio of n-hexane to methanol in the overhead product removed from the fractionation system. If the composition of this overhead product is equivalent to that of the azeotrope of n-hexane and methanol, said ratio must be maintained at a value between about 2.2:1 and 2.5:1. If the ratio is thus strictly controlled, a bottom product may be obtained which is free from methanol. However, a fractionating column having a considerably greater number of trays will be required than that utilized for the azeotropic distillation with an excess of methanol. Choice of the two ways of operating will be made with due regard for the economics involved, balancing the cost of separating excess methanol from the methyl cyclopentane against the cost of the added trays, etc.

Furthermore, if substantially pure n-hexane and/or methyl cyclopentane are not required, operating in a less efficient column or with a much lower reflux ratio, but otherwise under the conditions disclosed herein, may be done so as to give a more or less impure top and/or bottom product more efficiently and economically than would be accomplished without practicing the teachings of my invention. The purity required will be governed by commercial considerations.

Turning now to the drawing, a natural gasoline or other complex hydrocarbon mixture containing methyl cyclopentane and n-hexane, is led via line 1 into fractionator 2, where it is divided into a bottom product which leaves via line 3, and a top product of methyl cyclopentane, n-hexane, and lighter hydrocarbons, which passes via line 4 into fractionating column 5. In column 5, material boiling below n-hexane is taken off overhead through line 6, leaving n-hexane and methyl cyclopentane as a kettle product, which in turn is continuously led via line 7 into azeotrope column 8.

Methanol, which is to act as the entrainer, may pass into column 8 at different points, some coming from line 31 through line 9 for admixture with the charge stock in line 7 and/or through line 18 into the lower part of the column, and some entering near the top of the column from line 10 and/or line 11 as reflux. The methanol thus entering the column as reflux usually has some n-hexane in it as will be seen from the description below, while the methanol from line 31 generally is free from hydrocarbons. Condenser 11A is used to condense any amount of the overhead product which it may be desired

to use as reflux, which is then passed to column 8 through line 11 as described. However, all of the reflux may sometimes be supplied from line 10. A steam coil or other heating means is, of course, used for supplying heat to the bottom of column 8. The necessary temperatures, pressures, and other operating conditions in column 8 have already been disclosed in detail. N-hexane and methanol pass off overhead from column 8 through line 12. The composition of this overhead material will generally correspond to the azeotrope of n-hexane with methanol, although in some cases the overhead may be richer in methanol. In this case, the preferred upper top temperature limit of about 195° F. may be raised by as much as 15 or 20° F. A kettle product of methyl cyclopentane and methanol leaves through line 13 and passes through cooler 14 to line 15, whence it goes for further treatment to remove methanol, as will be described later. In case the proportion of methanol to charge stock should be so regulated that all of the n-hexane would pass off overhead through line 12 along with all of the methanol, the methyl cyclopentane would leave the bottom of the column through line 13 free from any methanol.

After passing through cooler 16, which is interposed in line 12, the cooled n-hexane-methanol mixture enters separator 17 and separates into an upper hydrocarbon-rich layer and a lower methanol-rich layer, which lower layer is taken via line 10 for re-introduction into column 8. The upper layer of n-hexane with methanol dissolved therein passes via line 19 into line 20. Also entering line 20 is a stream of water from line 21A. The mixture of n-hexane, methanol, and water passes through a centrifugal contactor 22 interposed in line 20, for thorough mixing, and thence to separator 23, wherein the n-hexane practically entirely free from methanol and water, is separated as an upper phase which is finally passed to storage or further use via line 24.

The methanol-water lower layer in separator 23 is sent to fractionator 25 via line 26. A separation of methanol from water is readily made in column 25, with the methanol passing overhead through line 27 and condenser 28 to accumulator 29, and the water passing from the kettle via line 21 to lines 21A and 21B. By means of line 30, methanol is then passed to line 31 through which it flows for re-use in azeotrope column 8. Line 30 also connects with line 32 which leads to the top of column 25 for supplying reflux. Make-up methanol may be brought into the system through line 33. Column 25 is provided with a heating unit in the form of a steam coil or the like. Line 40 supplies make-up water to the system.

Returning to the methyl cyclopentane and methanol in line 15, this mixture is mixed in centrifugal contactor 34 with water, which enters line 15 from line 21B. The mixture then passes from contactor 34 via line 35 to separator 36 and therein separates into two layers. The lower methanol-water layer is passed via line 37 to junction with line 26, and thus goes into methanol column 25 for separation into methanol and water. The upper layer in separator 36, which is essentially methyl cyclopentane free from water, methanol, and n-hexane, is passed by way of line 38 to storage or to blending tanks.

In case the heretofore-described proportioning of methanol and n-hexane entering column 8 is carried out so as to produce a bottom product in line 13 free from methanol, the water-contacting

and methanol-removing system may be by-passed from a point in line 15 prior to entry of line 21B around to line 38 by means of line 39.

Various pumps are shown in the drawing where needed for maintaining flow of liquids or for increasing or maintaining pressures at the required values. Valves for controlling pressures, and volumes of material, are not shown in the drawing, their use to maintain the required conditions of this invention being within the skill of the art.

Considering now in more detail the various steps used in separating the methanol and recycling it through the system, the following points may be emphasized. At temperatures above about 94° F., I have found that n-hexane and methanol are miscible in all proportions. Accordingly, I cool the overhead product from the azeotrope column to a temperature somewhat below this value, for example, to 85 or 90° F., and thus cause two layers to form in the separator 17. This formation of two layers accomplishes a great deal of separation as will be evident from Table I.

TABLE I
Solubility of n-hexane in methanol

Temperature, ° F.	Volume per cent N-hexane	
	N-hexane layer	Methanol layer
32.....	94.0	26.0
45.....	92.6	30.0
55.....	92.1	35.7
70.....	89.7	39.8
80.....	88.1	44.0
90.....	82.5	56.5

As previously described, the methanol layer is recycled to the column, preferably as reflux. If desired, a small percentage of water may be present in the methanol used in the azeotrope column.

The n-hexane layer still contains appreciable amounts of methanol, which it is desirable to remove. I have found that only a very small quantity of water need be mixed with this n-hexane-rich layer in order to reduce the methanol content from about 10 or 15 per cent to less than 0.1 per cent. I generally add about 1/3 volume of water for each volume of methanol present, which means that the water content of the n-hexane-methanol-water mixture need be only about from 3 to 5 per cent or even less. A short, vigorous agitation followed by settling is all that is required to separate in separator 23 a layer of substantially pure n-hexane and a layer of methanol and water.

The methanol from this last-named layer may be readily recovered by distillation from the water for re-use in the process because unlike the homologs of methanol, i. e., ethanol, propanol, etc., methanol does not form azeotropes with water. A suitable fractionating column for making this separation is one having 20 trays, roughly equivalent to about 13 theoretical plates, and operated at a reflux ratio of about 1 or 2 to 1. The methanol overhead from the methanol-water column is recycled to provide sufficient methanol in the azeotrope column 8 to maintain the desired methanol-hydrocarbon ratio.

I have found that a mixture of methyl cyclopentane with methanol must be cooled to about 55° F. in order to accomplish the separation of two phases. Even this may be impossible if there is a large excess of one or the other component.

Such a temperature cannot ordinarily be obtained with the cooling water usually available at a commercial installation. Therefore, unless propane refrigeration or the like is available at little cost, I find it best to mix water with the methyl cyclopentane-methanol mixture in order to free the desired methyl cyclopentane from methanol. As in the case of the n-hexane-methanol mixture, the volume of water required is relatively small, the hydrocarbon is freed of substantially all methanol and water, and the methanol and water are readily separated from each other by simple fractionation. However, as mentioned before, it may sometimes be more economical to produce a bottom product from the azeotropic distillation free from methanol in order to avoid the water washing, even at the expense of increasing the size of the azeotrope column. The choice, of course, will have to be decided in any individual case by taking the various factors into account, all in the light of the present disclosure.

It will be understood that the principles disclosed herein for a continuous process may be applied with suitable modifications to a batch process, and vice versa.

In order that the invention may be more readily understood, the following examples are offered. Example 1 relates to simple fractionation of a complex methyl cyclopentane- and n-hexane-containing hydrocarbon mixture. Example 2 discloses data obtained by using methanol according to the terms of the present invention. Example 3 gives data on the relation of reflux ratio to purity of product.

EXAMPLE 1

A technical hexanes fraction obtained from natural gasoline was carefully fractionated in a batch run in a specially constructed packed column 60 feet in height and having an efficiency equivalent to about 110 theoretical plates. A high reflux ratio was used, and equilibrium conditions obtained at all times. Data for selected cuts from this run are listed in Table II, while data for various pure hydrocarbons present in this hexanes cut are listed in Table III for comparison. The Fenske boiling range was obtained at 760 mm. Hg pressure in an apparatus as described by Quiggle, Fenske et al., Ind. Eng. Chem., Anal. Ed., 6, 466 (1934).

TABLE II

Fractionation of technical hexanes in 110-plate column

Volume per cent distilled overhead	Fenske B. R., ° F.		n_D^{20}	° A. P. I. @ 60° F.	Principal component
	Initial boiling point	Dry point			
1.833.....	93.7	93.1	-----	92.8	n-Pentane.
5.010.....	120.3	122.1	-----	62.0	Cyclopentane.
9.37.....	140.2	140.5	1.37247	83.5	2-methyl pentane.
15.12.....	140.3	140.4	1.37173	83.6	Do.
19.76.....	140.3	140.4	1.37157	83.6	Do.
25.1.....	140.4	140.4	1.37175	83.6	Do.
29.7.....	141.1	141.6	1.37193	83.4	Do.
34.82.....	144.5	144.8	-----	80.9	3-methyl pentane.
40.0.....	145.8	145.8	1.37649	80.2	Do.
45.4.....	146.4	147.2	1.37715	80.0	Do.
49.9.....	155.6	155.8	1.37818	80.0	Do.
55.3.....	155.6	155.8	1.37729	80.0	n-Hexane.
59.6.....	155.8	155.8	1.37760	79.9	Do.
64.9.....	155.9	156.0	1.37808	80.0	Do.
70.2.....	156.0	156.1	1.37864	79.6	Do.
73.4.....	156.0	156.1	1.37890	79.6	Do.
74.8.....	156.1	156.3	1.37943	79.0	Do.
77.7.....	157.1	157.4	1.38840	72.0	Do.
81.0.....	160.7	161.0	1.41270	56.5	Methyl cyclopentane.
Kettle bottoms unrecovered.	162.0	175.0	1.41569	54.9	Methyl cyclopentane (over-all loss).

TABLE III

Physical properties of pure hydrocarbons

Hydrocarbon	Boiling point, ° F.	n_D^{20}	° A. P. I. @ 60° F.
n-Pentane.....	96.9	1.3577	92.7
2-methyl pentane.....	140.4	1.3715	83.6
3-methyl pentane.....	145.8	1.3765	80.1
n-Hexane.....	155.8	1.3760	81.6
Cyclopentane.....	120.7	1.4068	57.1
Methyl cyclopentane.....	161.2	1.4098	56.4
Cyclohexane.....	177.3	1.4263	49.4
Benzene.....	176.2	1.5012	30.4

An examination of Tables II and III reveals that at first a slight quantity of n-pentane was distilled off at about 2% overhead, followed by a small amount of cyclopentane at about 5% overhead. From about 10% overhead to about 30 to 35% overhead, 2-methyl pentane was taken over, with the product from 15 through 25% overhead being pure 2-methyl pentane. From about 35 to about 45% overhead the product was 3-methyl pentane, with that coming off at around 40% overhead being pure 3-methyl pentane. From about 45 to about 75% overhead, the product was predominately n-hexane, but it will be noted that no pure n-hexane was produced. Up through 70% overhead, the bulk of the product was not more than 90% n-hexane, calculated from the refractive index and from the A. P. I. gravity. The best fraction was that at 55% overhead which contained 8% of methyl cyclopentane.

At about 75% overhead, the n-hexane had been almost all distilled off, and the overhead product from 78 to 81%, as well as the kettle bottoms, was predominately methyl cyclopentane, being contaminated with n-hexane, and later being contaminated with higher-boiling cyclics, perhaps cyclohexane and/or benzene.

Thus, the n-hexane obtainable by this very efficient fractionation was generally less than 90% pure, and at best 92% pure. Accordingly, about 10% of the n-hexane fraction represented a loss of unrecoverable methyl cyclopentane.

EXAMPLE 2

A normal hexane concentrate separated from natural gasoline by close fractionation and having a Fenske boiling range of 1° F. (156-157° F.) and an ASTM octane number of 50, was frac-

tionated batchwise in the presence of methanol to separate out substantially pure n-hexane and methyl cyclopentane, as described below.

A packed column 20 feet in height and having an efficiency equivalent to about 35 theoretical plates was used. The kettle capacity was 100 gallons. Pressures maintained in the still were from 17 to 30 pounds per square inch gage. Top temperatures were from 155 to 176° F. The reflux ratio was held at from 25:1 to 60:1.

At the start of the fractionation the kettle was charged with 36.3 gallons of the n-hexane concentrate and 25.4 gallons of methyl alcohol. Heat was applied, the pressure was allowed to build up, and the column was operated under total reflux until equilibrium was established. Product was thereafter drawn off overhead at a rate of about 0.5 gallon of hydrocarbon per hour. Data for selected cuts from this run are listed in Table IV. The percentage and properties referred to are for the hydrocarbon fractions after removal of methanol by water washing.

TABLE IV

Distillation with methanol of n-hexane concentrate in 35-plate column

Volume per cent distilled overhead	Fenske B. R., °F.		n _D ²⁰	°A. P. I. @ 60° F.
	Initial boiling point	Dry point		
5.0.....	154.9	155.8	-----	80.4
10.0.....	156.1	156.5	-----	80.5
15.0.....	155.7	156.0	-----	80.3
20.0.....	155.7	156.0	-----	80.4
25.0.....	155.9	155.9	-----	80.4
30.0.....	155.8	156.0	-----	80.0
35.0.....	155.6	156.1	-----	80.0
40.0.....	155.9	156.2	-----	79.9
45.0.....	155.9	156.2	-----	79.7
50.0.....	155.8	156.3	-----	79.5
55.0.....	156.0	157.5	-----	79.3
60.0.....	155.9	156.7	-----	78.9
65.0.....	155.8	156.7	-----	78.3
70.0.....	156.3	156.7	-----	77.8
75.0.....	156.3	156.8	-----	76.7
80.0.....	156.7	158.7	-----	74.0
84.5.....	157.6	159.4	-----	70.1
Kettle bottoms.....	159.6	163.3	1.4136	56.3
Blend of 5-25%.....	156.0	156.3	1.3760	80.4
Blend of 25-58%.....	156.0	156.3	1.3783	79.4

Reference to Tables IV and III shows that the product from 5 to 25% overhead was 97 per cent n-hexane, in contrast to the best n-hexane, 92%, which could be produced by straight fractionation in a column three times as efficient, as described in Example 1. The product from 25 to 58% overhead was 89 per cent n-hexane, or of about the same purity as the bulk of the n-hexane produced by fractionation in the much more efficient column of Example 1. The fractionation in the presence of methanol was continued until tests showed that the kettle contents were free from n-hexane. During this time the percentage distilled overhead increased to 84.5%.

The kettle product was a narrow-boiling naphthenic hydrocarbon fraction which, after washing with water, was found to be free of all n-hexane, and to comprise substantially pure methyl cyclopentane. It did contain small amounts of other cyclics, probably cyclohexane, and perhaps a trace of benzene, which were present due to incomplete separation occurring when the n-hexane concentrate was first prepared by fractionation from natural gasoline. The kettle product was 15.5 volume per cent of the charge. The ASTM octane number relationships of this kettle product were substantially identical to those of pure methyl cyclopentane, as shown in Table V.

TABLE V

ASTM octane numbers

CC. tetraethyl lead per gallon	Kettle bottoms	Methyl cyclopentane
0.0	79.9	80.5
1.0	87.7	88.2
3.0	91.9	92.3

It should be emphasized that a column of 35 theoretical plate efficiency as used for this batch distillation with methanol, could hardly be expected to produce sharp separation between close-boiling hydrocarbons and/or azeotropes, yet n-hexane was separated by the aid of methanol under the given conditions of temperature, pressure, and reflux ratio, in a purity of 97 per cent, which means that very little loss of methyl cyclopentane occurred. It will be appreciated by those skilled in the art that an increase in purity of from 92 to 97 per cent is such that the separation is of great significance, and represents a signal accomplishment.

The separation of substantially pure n-hexane and substantially pure methyl cyclopentane from a mixture containing the same has thus been accomplished in a simple and economical manner. Under a continuous method of operating, as described with reference to the drawing, this separation may be maintained throughout a run.

EXAMPLE 3

An azeotropic fractionation similar to that of Example 2 was carried out in a column of moderate efficiency and the reflux ratio was varied over a wide range, equilibrium being established after each change in ratio. The methanol-rich layer obtained by cooling overhead product was passed back into the fractionation system. Data obtained are given in Table VI.

TABLE VI

Effect of reflux ratios on purity of product

Reflux ratio	Per cent n-hexane in hydrocarbon portion of overhead
0.....	168.0
2.5:1.....	77.0
4.3:1.....	79.5
17.3:1.....	84.5
22:1.....	91.0
63:1.....	92.5
86:1.....	93.5

1 Composition of hydrocarbon charge.

Examination of Table VI reveals that a reflux ratio of less than about 20:1 produced quite an impure product, with the purity falling rapidly as the reflux ratio decreased. On the other hand, a reflux ratio of above about 20:1 gave an overhead product of greatly increased purity; however, the rate of increase in purity as the reflux ratio was increased was small, the purity increasing from 91 per cent at 22:1 ratio to 93.5 per cent at 86:1 ratio, which was near the maximum purity obtainable in the particular column being used.

Inasmuch as numerous other examples could be given, it will be understood that the invention is not at all limited by the specific examples offered, but only by the required conditions set forth in the specification and appended claims.

I claim:

1. A process for the separation of n-hexane and of methyl cyclopentane from a mixture containing the same which comprises fractionating said mixture in the presence of sufficient methanol to act as an azeotrope-forming agent, at a distillation pressure of at least about 10 pounds per square inch gage, and recovering a low-boiling fraction enriched in n-hexane and a higher-boiling fraction enriched in methyl cyclopentane.

2. A process for the separation of n-hexane and of methyl cyclopentane from a mixture containing the same by azeotropic distillation with methanol which comprises fractionating said mixture in the presence of substantial amounts of methanol at a distillation pressure above about 10 pounds per square inch gage and at a temperature above about 140° F., and recovering a low-boiling fraction enriched in n-hexane and a higher-boiling fraction enriched in methyl cyclopentane.

3. A process for the separation of n-hexane and of methyl cyclopentane from a mixture containing the same by azeotropic distillation with methanol which comprises fractionating said mixture in the presence of substantial amounts of methanol at a pressure in the range of about 10 to about 50 pounds per square inch gage and at a temperature in the range of about 140 to about 195° F., and recovering a low-boiling fraction enriched in n-hexane and a higher-boiling fraction enriched in methyl cyclopentane.

4. A process for producing concentrates of n-hexane and of methyl cyclopentane from a mixture of the same which comprises fractionally distilling said mixture with methanol at a distillation pressure above about 10 pounds per square inch gage and at a temperature above about 140° F., recovering top and bottom products containing hydrocarbon and methanol, and removing methanol from said top and bottom products to obtain hydrocarbons enriched in n-hexane and in methyl cyclopentane respectively.

5. A process for the separation of n-hexane and of methyl cyclopentane in substantially pure form from a mixture of the same which comprises fractionating said mixture in the presence of sufficient methanol to give a liquid volume ratio of n-hexane to methanol substantially less than about 2.2 to 1, in a fractionation system of at least about 35 theoretical plates, at distillation pressures about about 10 pounds per square inch gage and at temperatures above about 140° F., using a reflux ratio of at least about 20 to 1, recovering a low-boiling n-hexane fraction and a higher-boiling methyl cyclopentane fraction, and removing methanol from recovered hydrocarbon.

6. A continuous process for the separation of methyl cyclopentane from n-hexane by fractionation of a mixture comprising methyl cyclopentane and n-hexane in the presence of methanol, which comprises carrying out said fractionation at about 10 to about 50 pounds per square inch gage pressure and at about 140 to about 195° F., continuously removing an overhead methanol and n-hexane fraction from the fractionation system, continuously removing a methyl cyclopentane bottom product substantially free from n-hexane and methanol, and continuously supplying methanol in such proportions that the ratio of methanol entering the system to n-hexane entering the system is substantially equal to the ratio of methanol to n-hexane in said overhead fraction.

7. A process for recovering n-hexane from a substantially constant-boiling mixture with methyl cyclopentane, which comprises distilling said mixture with sufficient added methanol to effect substantial separation of said n-hexane from methyl cyclopentane in a fractionation column at pressures between about 10 and about 50 pounds per square inch gage and at top temperatures of about 140 to about 195° F., withdrawing an azeotropic mixture of n-hexane and methanol from the top of said column, separating methanol from said azeotropic mixture, and thereby obtaining n-hexane.

8. A process for continuously effecting separation between n-hexane and methyl cyclopentane which comprises continuously introducing a hydrocarbon mixture containing substantially only n-hexane and methyl cyclopentane into a fractionator, continuously introducing methanol into said fractionator in the ratio of one liquid volume of methanol to from about 2.2 to about 2.5 liquid volumes of n-hexane, distilling the contents of said fractionator at from about 10 to about 50 pounds per square inch gage and with a top temperature of from about 140 to about 195° F., and continuously removing an overhead product comprising predominately an azeotrope of n-hexane and methanol and a bottom product comprising predominately methyl cyclopentane.

9. In a continuous process for the separation of a mixture of methyl cyclopentane and n-hexane into its components by azeotropic distillation with methanol, the steps which comprise introducing said mixture into a fractionation zone, fractionating the same therein with methanol introduced as hereinafter described at distillation pressures above about 10 pounds per square inch gage and at temperatures above about 140° F., removing a bottom product comprising methyl cyclopentane, cooling overhead product comprising n-hexane and methanol from said zone to a temperature below about 94° F. to separate a n-hexane-rich phase and a methanol-rich phase, returning said methanol-rich phase to the fractionation zone to furnish at least a portion of the reflux, and introducing into said fractionation zone an additional amount of methanol substantially equal in quantity to that dissolved in said n-hexane-rich phase plus any dissolved in said bottom product.

10. A process for continuously producing n-hexane and methyl cyclopentane which comprises introducing a mixture thereof into a fractionator, introducing methanol into said fractionator, operating said fractionator at a distillation pressure above about 10 pounds per square inch gage, withdrawing n-hexane and methanol from the top of said fractionator at a temperature above about 140° F., cooling at least a portion of said n-hexane and methanol to below about 94° F. and passing to a separating zone to form two liquid layers, returning to the fractionator the lower layer from said separating zone, returning to the top of said fractionator at least about 20 liquid volumes of total reflux per volume of n-hexane separated from the fractionating system, withdrawing methyl cyclopentane and methanol from the fractionator as bottom product, separating n-hexane from the fractionating system by passing material from the upper layer from said separator first to intimate admixture with water and then to a first settling zone, said water being at least about one-third the volume of the methanol contained in said material from the upper layer, withdrawing from

said first settling zone a substantially methanol-free n-hexane phase, passing said bottom product first to intimate admixture with water and then to a second settling zone, said water being at least about one-third the volume of the methanol in said bottom product, withdrawing from said second settling zone a substantially methanol-free methyl cyclopentane phase, passing the methanol-water phases from said first and second settling zones to a distillation unit, distilling methanol as top product and water as bottom product from said unit, recycling said methanol to the fractionator, and recycling a portion of said water to contact with said material from the upper layer from the aforementioned separator and a portion of said water to contact with said bottom product.

11. A process for the separation of methyl cyclopentane and of n-hexane in substantially pure form from a complex hydrocarbon mixture containing the same which comprises separating by fractional distillation a substantially constant-boiling mixture comprising essentially n-hexane and methyl cyclopentane, admixing methanol with said constant-boiling mixture, and fractionating the resulting mixture at a pressure from about 10 to about 50 pounds per square inch gage and at a temperature from about 140 to about 195° F. to separate overhead from methyl cyclopentane substantially all the n-hexane as an azeotrope with methanol.

12. A process for the production of a high-octane number aviation fuel blending stock comprising essentially methyl cyclopentane which comprises fractionating a natural gasoline containing methyl cyclopentane and n-hexane to remove heptanes and heavier, deisohexanizing the

resulting product to produce a n-hexane-methyl cyclopentane fraction of narrow boiling range, fractionating said fraction in the presence of methanol at a pressure in the range of about 10 to about 50 pounds per square inch gage to take off substantially all the n-hexane as an azeotrope with methanol at an overhead temperature in the range of about 140 to about 195° F., and recovering as bottoms a high-octane number stock comprising essentially methyl cyclopentane.

13. A process for producing a narrow-boiling naphthenic hydrocarbon fraction boiling in the range of about 161° F. at standard atmosphere pressure, having a gravity at 60° F. of about 56° A. P. I., having a refractive index of about 1.41, and having an ASIM octane number of about 80 with no added tetraethyl lead, of about 88 with 1 cc. tetraethyl lead per gallon, and of about 92 with 3 cc. tetraethyl lead per gallon, which process comprises depentanizing a natural gasoline containing methyl cyclopentane, deisohexanizing the depentanized gasoline, fractionating the deisohexanized gasoline to produce a narrow-boiling naphthene-containing n-hexane fraction overhead and a heptanes and heavier kettle product, fractionating the n-hexane fraction with methanol in a column equivalent to at least about 35 theoretical plates, with a reflux ratio of at least about 20 to 1, at a distillation pressure of at least about 10 pounds per square inch gage, and at a top temperature of at least about 140° F., along with at least sufficient methanol to permit substantially complete separation of n-hexane overhead as an azeotrope with methanol, and recovering the desired narrow-boiling naphthenic fraction from the kettle.

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