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PROCESS FOR SEPARATING CYCLOPENTENE FROM PIPERYLENE

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This invention relates to a process for the separation of mixtures of olefins of different types, or of olefins and paraffins, containing five to seven carbon atoms per molecule, into two or more portions having different properties or containing hydrocarbons of different types. By olefins I refer to hydrocarbons containing at least one olefinic linkage, that is a double bond between carbon atoms, which may be described more specifically as mono-olefins, diolefins, or cyclic olefins. More particularly, this invention relates to the use of methanol in order to render separation into hydrocarbon types by fractional distillation much more practical and feasible than by simple fractional distillation alone.

Hydrocarbon mixtures of a complex nature are produced in various petroleum cracking processes and in other ways. In order to best utilize certain components of such mixtures, it is frequently desirable to isolate or recover these components in concentrated form. Thus, it is frequently desirable to utilize pentenes in a substantially concentrated form for the manufacture of pentadienes; similarly, it is desirable to separate the resulting pentadienes from the unreacted pentenes. Although no difficulty is experienced in preparing a hydrocarbon fraction by conventional fractional distillation that will have a relatively narrow boiling range and that will contain for the most part hydrocarbons having the same number of carbon atoms per molecule, further segregation of the hydrocarbons is difficult if not impossible to achieve by ordinary fractionation.

There are a number of instances among the five-, six-, and seven-carbon olefin and paraffin hydrocarbons in which two or more hydrocarbons of different types are quite near-boiling. As commercially important instances may be mentioned the following:

Hydrocarbon	Boiling point, °F.
A. Pentene-2 (low-boiling isomer)	96.6–97.5
n-Pentane	97.0
Pentene-2 (high-boiling isomer)	98.6
B. Piperylene (high-boiling isomer)	111.5
Cyclopentene	111.6–112.0
C. Hexene-2 (mixture of isomers)	154–156
n-Hexane	155.8

In these examples of close-boiling hydrocarbons, it will be readily understood that the differences in boiling points within each example are too small for commercially feasible separations of the hydrocarbons by conventional fractionation. Furthermore, certain cases exist in which hydrocarbons of different types form constant-boiling mixtures, and in these cases separation of the hydrocarbons by ordinary fractionation under the usual conditions is impossible. Such is true, I have found, of mixtures of cyclopentene and piperylene.

It is an object of my invention to provide a process for the separation of close-boiling hydrocarbon mixtures containing more than one type of compound into fractions having different compositions. A further object of my invention is to provide a method for separation by azeotropic distillation of five carbon atom hydrocarbons of different types, namely diolefins, and cyclo-olefins from mixtures of two or more of such hydrocarbons having relatively close boiling points, whereby one or more of the different hydrocarbons may be concentrated, or separated in substantially pure form. Another object of my invention is to provide an entraining agent for use in the distillation of such hydrocarbon mixtures to aid in the separation of the different hydrocarbons one from the other. A specific object of my invention is to separate cyclopentene and piperylene from a material containing the same and from each other.

My invention is a process for the separation, into two or more fractions of different composition, of hydrocarbon mixtures that may contain two or more 5 to 7-carbon atom paraffins and/or olefins, including cyclopentene and piperylene. The process consists in fractionally distilling the hydrocarbon mixtures in the presence of methanol, which forms minimum-boiling azeotropic mixtures with the several hydrocarbons. I have found that in general the addition of suitable amounts of methanol to a mixture of a paraffin and a mono-olefin that have like boiling points results in so changing the relative volatilities of the paraffin and mono-olefin that upon fractional distillation the overhead product is found to have a higher paraffin-mono-olefin ratio than the original mixture. Thus, although the addition of methanol to a pure paraffin or a pure mono-olefin results in the formation of a minimum-boiling azeotropic mixture in each case, there is in general a greater increase in the apparent volatility of the paraffin than in that of the mono-olefin. A similar effect is found for paraffins and diolefins, in that the addition of methanol results in a greater enhancement of the volatility of paraffins than of that of diolefins. I have further found that the presence of methanol results in enhancing the relative volatility of mono-olefins and cyclo-olefins in comparison with that of di-

olefins. Accordingly, it may be said that in general the more saturated hydrocarbon is concentrated in the overhead product, and the less saturated is concentrated in the kettle product. In this way, I may use methanol to separate like-boiling olefins, that is mono-olefins, diolefins, and/or cyclo-olefins, one from the other or from paraffins.

I may apply my process to a variety of hydrocarbon mixtures. In general I prefer to treat relatively narrow-boiling mixtures such as might result from a preliminary conventional fractional distillation. In order to obtain maximum efficiency in practicing my process of azeotropic distillation, it is desirable that the hydrocarbon mixture contain not more than minor amounts of hydrocarbons boiling more than about 4° to 6° F. above the olefin in the mixture that is to be produced as a kettle product. No such limitation is involved, however, so far as the presence of hydrocarbons boiling considerably below the olefin or olefins to be produced as a kettle product is concerned.

As will be understood by those skilled in the art, the many different ways of carrying out azeotropic distillations which are known to the art may be applied with suitable modification, in view of this disclosure, to carry out the present invention. Thus, batchwise fractional distillation may be utilized in practicing my process, or continuous fractionation may be employed. In the latter case, the hydrocarbon mixture is continuously charged to the fractionating column at some point along the column, and the methanol entrainer is added at the same point or at some other point or points along the column. In such a continuous fractionation, a product comprising one or more olefins is ordinarily removed from the kettle of the column, and an azetropic mixture of one or more other hydrocarbons with the methanol is taken off the top of the column. The olefins removed from the kettle may or may not contain substantial amounts of the methanol, depending upon the relative amounts of entrainer and hydrocarbon mixture charged to the column, and my process may be operated with any desired ratio of methanol to hydrocarbon mixture equal to or greater than a minimum ratio which will be determined by the amount of methanol required to form azeotropic mixtures with the hydrocarbon or hydrocarbons which are to be distilled overhead. If desired, minor proportions of water, preferably less than about 5 per cent, may sometimes be used in the azeotrope column along with the entrainer to aid the selective action of the methanol.

In operating my process, I use any convenient method of removing the methanol from the products of the fractionation, such as water washing. The methanol thus separated from the hydrocarbons may then be recovered in known fashion such as by simple fractional distillation, and returned to the azeotrope column.

The pressure at which my process is most conveniently operated depends upon the volatility of the hydrocarbon mixture being distilled. Thus, in fractionating five-carbon hydrocarbon mixtures, pressures up to around 50 pounds per square inch gauge are usually desirable, whereas in fractionating six- and seven-carbon hydrocarbon mixtures pressures near atmospheric are advantageously employed. However, if desired, pressures higher than these may be used.

In order further to illustrate and describe my invention, I may cite the following examples, without, however, limiting the invention thereto.

EXAMPLE I

A mixture of n-pentane and pentene-2 having a specific gravity (20/20) of 0.6361 and an estimated pentene-2 content of about 37 per cent, together with methanol in a hydrocarbon-to-methanol volume ratio of 200:155, was subjected to batchwise fractionation at atmospheric pressure in a column of 1.2-cm inside diameter packed to a height of 120 cm with $\frac{1}{16}$-inch diameter single-turn wire helices. A reflux ratio of about 75:1 was employed. The course of the distillation is shown in Table I.

TABLE I

Pentene-2—N-pentane separation by azeotropic fractionation with methanol

Fraction	Boiling range (corrected to 760 mm.)		Entrainer in overhead vol. percent	Vol. percent of charge	Cumul. vol. percent of charge	n_D^{20}	Sp. gr. 20/20	Percent pentene-2 in fraction	
	° F.	° C.						By sp. gr. 20/20	By Br₂ titr.
				(Methanol-free)					
1	86.5–87.1	30.3–30.6	15.0	14.0	14.0	1.3600	0.6298	10	13
2	87.1–87.3	30.6–30.7	11.1	16.0	30.0	1.3601	0.6301	11	
3	87.3	30.7	13.0	13.5	43.5	1.3606	0.6305	13	
4	87.3	30.7	13.5	16.0	59.5	1.3616	0.6314	17	20
5	87.3–88.5	30.7–31.4	15.0	14.0	73.5	1.3693	0.6392	50	
6	88.5–88.9	31.4–31.6	12.0	11.0	84.5	1.3785	0.6492	93	
Loss				15.5	100.0				
Avg.			12						

The boiling points of fractions 1 and 6 (Table I), after removal of methanol by water washing, were determined with a Cottrell boiling point apparatus and were found to be as follows:

Fraction	Boiling point (760 mm.)
	° F.
1	96.6
6	97.3

In this application of my invention, efficient separation of the two types of hydrocarbons, paraffins and mono-olefins, was realized in spite of the fact that only a minute difference in the boiling points of the hydrocarbons exists. It is practically impossible to effect a comparable separation by the methods of conventional fractional distillation.

EXAMPLE II

An extremely close-cut hexane-hexene fraction, distilling at corrected temperatures (760 mm. mercury) of 153.7° to 154.8° F. and contain-

ing 50.4 mole per cent mono-olefins by bromine titration, was subjected together with a volume of methanol equivalent to 139 volume per cent of the hydrocarbon charge, to batchwise fractionation at atmospheric pressure in the column described in Example I. A reflux ratio of about 70:1 was employed. The course of the distillation is shown in Table II.

TABLE II

Hexene—N-hexane separation by azeotropic fractionation with methanol

Fraction	Boiling range (corrected to 760 mm.)		Entrainer in overhead, vol. per cent	Vol. per cent of charge	Cumul. vol. per cent of charge	n_D^{20}	Sp. gr. 20/20	Per cent hexenes in fraction by bromine titration
	° F.	° C.						
				(Methanol-free)				
1	121.1	49.5	27.4	20.5	20.5	1.3797		26.4
2	121.3	49.6	25.0	25.0	45.5	1.3813		32.4
3	121.8	49.9	27.1	23.9	69.4	1.3851		50.4
4	122	50.0	26.0	20.5	89.9	1.3950	0.6817	96.0
5	122—131	50.0—55	70	6.7	96.6	1.4020		96.0
Loss				3.4	100.0			
Avg			[1] 26.4					

[1] Exclusive of value for fraction 5.

Since the original hexane-hexene cut contained 50 mole per cent olefins, it is seen from Table II that more than half of the hexenes was recovered in 96 per cent concentration by the application of my process. This result is the more remarkable since from consideration of the distilling temperature range of the hydrocarbons alone (that is, 153.7°–154.8° F.) it appears that the hexenes must have been predominantly 2-methyl pentene-2 and the isomers of hexene-2 and hexene-3, and these hexenes boil below n-hexane as indicated hereinbefore, whereas in the distillation these hexenes were concentrated in the less-volatile fractions, which were the last to distill over.

EXAMPLE III

By fractionation of the so-called light oils produced in pyrolysis of hydrocarbon gases, a fraction containing five-carbon hydrocarbons of various types was produced. This fraction was then subjected to further close fractionation in order to produce a fraction distilling at 110.8° to 111.6° F. (corrected to 760 mm. mercury) that had a specific gravity (20/20) of 0.7473 and that was composed of about 68 mole per cent cyclopentene and 32 mole per cent of the high-boiling isomer of piperylene. This latter fraction was then subjected to batchwise fractionation at atmospheric pressure in the presence of methanol amounting to 45 volume per cent of the hydrocarbon volume. The fractionating column described in Example I was used, and a reflux ratio of 70:1 was employed. The course of the azeotropic distillation with methanol is shown in Table III.

TABLE III

Azeotropic separation of cyclopentene from high-boiling piperylene with methanol

Fraction	Boiling range (corrected to 760 mm.)		Entrainer in overhead, vol. per cent	Vol. per cent of charge	Cumul. vol. per cent of charge	Sp. gr. 20/20	Per cent high-boiling piperylene in fraction by sp. gr. 20/20
	° F.	° C.					
				(Methanol-free)			
1	98.2–99.0	36.8–37.2	20	9.1	9.1	0.7565	20
2	99.0–99.2	37.2–37.3	17.7	12.7	21.8	0.7568	20
3	99.0–99.2	37.2–37.3	16.7	12.5	34.3	0.7562	21
4	99.0–99.2	37.2–37.3	16.7	12.5	46.8	0.7554	22
5	99.0–99.2	37.2–37.3	17.5	11.8	58.6	0.7542	23
6	99.0–99.5	37.2 37.5	15.7	17.1	75.7	0.7468	32
7	99.5	37.5	16.7	10.2	85.9	0.7019	88
Loss				14.1	100.0		
Average			17				

It is seen from Table III that about 25 per cent of the high-boiling isomer of piperylene that was contained in the hydrocarbon charge was recovered in fraction 7 in about 88 per cent purity. Even higher purity may readily be obtained by use of a more efficient fractionation column. Such a separation would be impossible to achieve by conventional fractionation on account of the tendency of the hydrocarbons involved to form a constant-boiling mixture, and even if this complication were absent the boiling points of the hydrocarbons are too close for satisfactory separation by ordinary means.

Because my invention may be practiced otherwise than as specifically shown herein, and because many modifications and variations of it will be obvious to those skilled in the art, it should not be restricted except as specifically indicated in the appended claims.

I claim:

1. The process of separating into its components a narrow-boiling-range mixture comprising cyclopentene and piperylene which comprises fractionally distilling said mixture in the pres-

ence of sufficient methanol to form an azeotrope with at least a substantial proportion of the cyclopentene in said mixture, separating a minimum-boiling hydrocarbon-methanol azeotrope containing said cyclopentene concentrated therein as a low-boiling product, and separating a higher-boiling product containing said piperylene concentrated therein.

2. The process of separating into its components a narrow-boiling-range mixture comprising cyclopentene and the high-boiling isomer of piperylene which comprises fractionally distilling said mixture in the presence of sufficient methanol to form an azeotrope with at least a substantial proportion of the cyclopentene in said mixture, separating a minimum-boiling hydrocarbon-methanol azeotrope containing said cyclopentene concentrated therein as a low-boiling product, and separating a higher-boiling product containing said piperylene concentrated therein.

3. A process for recovering concentrates of cyclopentene and of piperylene from an unsaturated hydrocarbon oil containing the same which comprises subjecting said oil to fractional distillation to produce a substantially constant-boiling mixture essentially comprising cyclopentene and piperylene, and fractionally distilling said mixture in the presence of at least sufficient methanol to form an azeotrope with all of said cyclopentene to concentrate said cyclopentene in an overhead fraction as a minimum-boiling azeotrope with methanol and to concentrate said piperylene in the residue.

4. The process of claim 1 further characterized by the presence of water during said fractional distillation in an amount less than about five per cent of said methanol but sufficient to aid the selective action of said methanol.

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