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PROCESS FOR PURIFYING NORMAL 1-OLEFINS

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This invention relates to a process for the purification of olefinic hydrocarbons. In one embodiment it relates to an improved method for the separation and recovery of certain isomeric olefinic hydrocarbons which are extremely difficult, if not impossible, to separate satisfactorily by fractional distillation. In one specific embodiment it relates to the removal of 2-methyl-1-butene from pentene-1, and the recovery of pure pentene-1.

In certain commercial processes for the production of individual olefinic hydrocarbons from petroleum fractions or the like, there is obtained a rather complex mixture of hydrocarbons whose normal boiling points fall within relatively narrow limits. For example, in the production of C_5 olefins from certain refinery streams it is found that (with one exception) the boiling points of all of the C_5 olefins fall within the range of approximately 86° F. to approximately 101° F. The sole exception is the compound 3-methyl-1-butene, boiling at 68.1° F. The boiling point of normal pentane also falls within the above-mentioned range. By means of highly efficient fractionation processes, this mixture of C_5 olefins can be separated into a high boiling fraction containing chiefly 2-pentene and 2-methyl-2-butene, and a low boiling fraction containing pentene-1 and 2-methyl-1-butene. The separation, by fractional distillation, of these latter two compounds is impracticable because their boiling points are within 2° F. of each other, pentene-1 boiling at 85.95° F. and 2-methyl-1-butene boiling at 87.98° F.

Because of the fact that such pentene-1 containing streams are desirable sources of this particular olefin, a satisfactory method for the removal of 2-methyl-1-butene from pentene-1 is greatly to be desired. If the pentene-1 is to be used in certain manufacturing processes in which the presence of olefins other than pentene-1 leads to the formation of undesired by-products, it becomes particularly important that the quantity of other olefins in the final pentene-1 product stream be minimized.

An object of this invention is to provide a process for the removal of close boiling isomeric olefins from the corresponding 1-olefins having at least four and preferably not more than ten carbon atoms per molecule.

Another object is to provide a process for the removal of isomeric olefinic hydrocarbons from pentene-1.

A further object is to provide a process for the production of pentene-1 in substantially pure

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form from C_5 hydrocarbons from cracked refinery streams.

Still another object is to provide a process for the removal of 2-methyl-1-butene from pentene-1.

Other objects and advantages will be apparent to one skilled in the art from the accompanying disclosure and discussion.

The process of this invention is particularly applicable to the separation and purification of pentene-1 from admixture with certain other olefinic hydrocarbons. In accordance with this invention, a pentene-1 containing stream is subjected to efficient fractional distillation to produce a fraction boiling in the range 85 to 88° F. and which contains 2-methyl-1-butene and lesser quantities of other olefins, such as 2-methyl-2-butene, in addition to pentene-1. This fraction is admixed with nitrosyl chloride in sufficient quantity and under conditions such that a reaction occurs between the nitrosyl chloride and the isomeric C_5 olefins present, but substantially no reaction occurs between the nitrosyl chloride and the pentene-1. The pentene-1 may then be recovered from the reaction mixture in substantially pure form by conventional distillation methods.

In one embodiment of the present invention a refinery stream containing C_5 olefinic and paraffinic hydrocarbons is subjected to efficient fractional distillation whereby pentene-1 is separated and concentrated into a fraction having a relatively narrow boiling range. The compound 2-methyl-1-butene, smaller amounts of normal pentane and isopentane, and traces of olefins of similar boiling range are contained in the pentene-1 fraction. The extent to which these compounds may be further separated by fractional distillations depends, of course, upon the efficiency of the fractionation process employed. Obviously, the substantially complete removal of the n-pentane (B. P. 96.93° F.) by highly efficient fractional distillation is within the realm of possibility. The separation of the isopentane (B. P. 82.14° F.) is much more difficult by this means, and the separation of the 2-methyl-1-butene (B. P. 87.98° F.) from pentene-1 (B. P. 85.95° F.) by fractional distillation is highly impracticable. Fortunately, for many of the intended uses of the pentene-1 the presence of minor amounts of paraffinic hydrocarbons, such as n- and isopentane, is of no consequence and their presence may be disregarded. As pointed out hereinabove, however, it is often essential that the pentene-1 be substantially free from other olefins. Accordingly, by the preferred embodiment of this invention the pentene-1 fraction is treated with nitrosyl chloride for the removal of the 2-methyl-1-butene and any other olefins (except pentene-1) that may be present. The gaseous nitrosyl chloride is preferably admixed with the liquid hydrocarbons in a suitable corrosion resistant reaction vessel equipped with stirring or agitating means and temperature control means. The rate of introduction of the nitrosyl chloride into the reaction mixture is preferably controlled so that no large excess of NOCl is present at any time. The presence of unreacted NOCl may readily be determined by reason of the brownish color imparted to the reaction mixture. The product of the reaction between NOCl and 2-methyl-1-butene imparts a greenish color to the mixture, the intensity depending upon the concentration of the reaction product present. The reaction temperature may be within the approximate range of 0 to 100° F., but is preferably maintained at from 60 to 80° F. in order to obtain a reasonably rapid rate of reaction without at the same time developing excessive pressures within the reaction vessel. Higher temperatures are to be avoided because they result in the decomposition of NOCl and chlorination of the hydrocarbons. Pressures sufficient to maintain the hydrocarbons in liquid phase are preferred. When the reaction between the 2-methyl-1-butene and NOCl is substantially complete, as evidenced by the persistence of the brownish color of unreacted NOCl in the reaction mixture, the products are separated by fractional distillation into unreacted nitrosyl chloride (B. P. 21.7° F.), pentene-1 (B. P. 85.95° F.) and the higher boiling reaction product of nitrosyl chloride with 2-methyl-1-butene and similar olefins. The pentene-1 fraction is washed with dilute aqueous sodium hydroxide or the like, and with water to remove traces of NOCl, and then dried by distillation if desired.

The step of treating the olefinic hydrocarbons with nitrosyl chloride may be carried out either continuously or batchwise, in any suitable apparatus adapted to maintain the hydrocarbon reactants in liquid phase and to provide efficient contacting of the hydrocarbons with the nitrosyl chloride at the desired temperature.

The present invention is particularly advantageous with respect to the high percentage recovery of 1-olefins, such as pentene-1, from an olefinic mixture containing such olefins, as compared with known methods for separating 1-olefins from such mixtures. It has been proposed, for example, to separate tertiary base olefins (such as 2-methyl-1-butene) from 1-olefin (such as pentene-1) by treatment of the hydrocarbons with 60–70% sulfuric acid under conditions such that the tertiary base olefin is polymerized or otherwise converted to higher boiling products. It has been found, however, that an appreciable loss of pentene-1 occurs under the conditions required for substantially complete removal of the 2-methyl-1-butene by the above-mentioned sulfuric acid treatment. In a typical run using 60 percent sulfuric acid and employing a contact time of 90 minutes, a pentene-1 concentrate containing 44.3 weight percent pentene-1 and 30.2 weight percent 2-methyl-1-butene (the remainder being chiefly normal and isopentane) was treated and it was found that the product contained 12 weight percent of pentene-2. This, of course, represents an undesirably high loss of pentene-1 due to isomerization. The nitrosyl chloride treatment of this invention, on the other hand, effects substantially complete removal of olefins of the type of 2-methyl-1-butene with almost no isomerization of, or reaction with, pentene-1, and hence makes possible a high degree of recovery of the latter compound.

Because of the reactivity of nitrosyl chloride with water, it is usually preferable to carry out the present invention under substantially anhydrous conditions. However, it has been found that in the presence of small amounts of water (1–2%) the rate of reaction of nitrosyl chloride with olefins is accelerated and that the degree of removal of 2-methyl-1-butene is even more nearly complete than when anhydrous conditions are employed. Since this is accomplished at the expense of pentene-1 (by reaction with NOCl), it is preferred to exclude water from the reactants, except when pentene-1 of extra high purity is to be produced.

In certain instances it may be desirable to conduct the NOCl treatment in two or more stages, with intermediate separation steps for the removal of the nitrosyl chloride-2-methyl-1-butene reaction product. Such a multiple stage process is advantageous, for example, when the pentene-1 stream contains a relatively large proportion of 2-methyl-1-butene.

While the process of the invention has been described with particular reference to the removal of 2-methyl-1-butene from pentene-1, for the sake of clarity, the invention is not limited to the purification of this particular olefin but may be successfully employed in the purification of other olefins. Thus, my process is applicable for the purification of straight or branched chain 1-olefins having the configuration

$$R-\overset{H}{\overset{|}{C}}=CH_2$$

where R is any alkyl radical having at least two and preferably not more than eight carbon atoms. Olefins having this configuration will be referred to in this specification and in the claims as secondary base 1-olefins. The secondary base 1-olefins are substantially unreactive with nitrosyl chloride. All olefins of any other configuration are relatively more reactive with nitrosyl chloride than are the corresponding secondary base 1-olefins. These other types of olefins will be referred to in the specification and the claims as non-(secondary base 1-olefins). This term is limited to olefinic hydrocarbons and is not intended to include other types of compounds that might be present, for example, the corresponding paraffin hydrocarbons. The olefins for which the process of my invention is particularly suitable are those having at least four and not more than ten carbon atoms per molecule; however in some cases olefins having up to twenty carbon atoms may be separated and purified by my process. Thus my invention may be employed in the separation of isobutylene (B. P. 19.58° F.) from butene-1 (B. P. 20.73° F.), certain hexenes (particularly hexene-2, hexene-3 and 2-methyl pentene-1) from hexene-1, and in general, in the separation of isomeric olefins from heptene-1, octene-1, etc. In the case of the higher boiling 1-olefins the temperature at which the NOCl treatment is carried out is preferably in the lower portion of the range indicated hereinbefore, say from 20° F. to 50° F.

Although nitrosyl chloride is the preferred reagent for use in this invention, nitrosyl bromide, NOBr, may be substituted in some cases provided that substantially lower temperatures are employed in the olefin treating step.

In order that the invention may be understood more fully, the following examples are given. It will be understood that these examples are given for illustrative purposes only, and are not intended to be limitations of the invention.

Example I

A mixture consisting of 80 percent by weight of pentene-1 and 20 percent by weight of 2-methyl-1-butene was placed in a glass reactor provided with a stirrer and a Dry-Ice condenser to which was added 20 percent by weight of nitrosyl chloride over a period of 3 hours at a temperature 75° F. The unreacted hydrocarbon was removed from the reaction product by distillation and was washed first with 5 per cent sodium hydroxide solution, then with distilled water. Upon distillation the hydrocarbon was found to have a refractive index (n_D^{20}) of 1.3715. The refractive index of the mixture prior to nitrosyl chloride treatment was 1.3728. Infrared analysis showed that the 2-methyl-1-butene content of the thus treated hydrocarbon had been reduced to about 5 weight percent by this single stage treatment.

Example II

A 100 gram sample of technical grade pentene-1 containing about 2.6 percent by weight of 2-methyl-1-butene as the sole olefinic impurity contained in a 300 cc. glass reactor provided with a stirrer and Dry Ice condenser was treated with a small excess of nitrosyl chloride based on the 2-methyl-1-butene present at 75° F. over a period of 1½ hours. The 2-methyl-1-butene content of the recovered hydrocarbon was reduced to 1.8 percent.

Example III

To 100 grams of 95% pure pentene-1 (n_D^{20}=1.3719) containing 2 grams of water contained in a 300 cc. glass reactor provided with a stirrer and a Dry-Ice condenser was added 8 grams of nitrosyl chloride over a period of 1 hour at 80% F. temperature. The refractive index of the recovered pentene-1 was found to be n_D^{20}=1.3712 which corresponds closely to that of the pure compound, n_D^{20}=1.3710.

It is to be understood that this invention should not be necessarily limited to the above discussion and description, and that modifications and variations may be made without departing from the invention and from the scope of the claims.

I claim:

1. A process for purifying a secondary base 1-olefin having from 4 to 5 carbon atoms from its admixture with a fraction selected from the class consisting of C_4 and C_5 hydrocarbons which comprises removing from said fraction a narrow boiling fraction comprising said secondary base 1-olefin and a corresponding hydrocarbon selected from the class consisting of isobutylene and 2-methyl-1-butene, treating said narrow boiling fraction with nitrosyl chloride in the presence of water in an amount within the range of 1 to 2 per cent by weight of said narrow boiling fraction at a temperature in the range between 0 and 100° F. and under a pressure sufficient to maintain a liquid phase, whereby the nitrosyl chloride reacts with said corresponding hydrocarbons and recovering secondary base 1-olefin from a resulting reaction mixture.

2. A process for purifying pentene-1 from its admixture with a C_5 fraction of hydrocarbon which comprises removing from said C_5 fraction a narrow boiling fraction comprising said pentene-1 and 2-methyl-1-butene, treating said narrow boiling fraction with nitrosyl chloride in the presence of 2 parts by weight of water per 100 parts of said narrow boiling fraction at a temperature in the range between 60 and 80° F. and under a pressure sufficient to maintain a liquid phase whereby the nitrosyl chloride reacts with 2-methyl-1-butene and recovering pentene-1 from a resulting reaction mixture.

3. A process for purifying pentene-1 from its admixture with a C_5 fraction of hydrocarbon which comprises removing from said C_5 fraction a narrow boiling fraction comprising said pentene-1 and 2-methyl-1-butene, treating said narrow boiling fraction with nitrosyl chloride in the presence of promoter quantities of water not exceeding 2 parts by weight of water per 100 parts of said narrow boiling fraction at a temperature in the range between 0 and 100° F. and under a pressure sufficient to maintain a liquid phase whereby the nitrosyl chloride reacts with 2-methyl-1-butene and recovering pentene-1 from a resulting reaction mixture.

4. A process for purifying pentene-1 from its admixture with a C_5 fraction of hydrocarbon which comprises removing from said C_5 fraction a narrow boiling fraction comprising said pentene-1 and 2-methyl-1-butene, treating said narrow boiling fraction with nitrosyl chloride in the presence of water in an amount within the range of 1 to 2 per cent by weight of the said narrow boiling fraction at a temperature in the range between 0 and 100° F. and under a pressure sufficient to maintain a liquid phase whereby the nitrosyl chloride reacts with 2-methyl-1-butene and recovering pentene-1 from a resulting reaction mixture.

5. A process for purifying butene-1 from its admixture with a C_4 fraction of hydrocarbon which comprises removing from said C_4 fraction a narrow boiling fraction comprising said butene-1 and isobutylene, treating said narrow boiling fraction with nitrosyl chloride in the presence of 2 parts by weight of water per 100 parts of said narrow boiling fraction at a temperature in the range between 60 and 80° F. and under a pressure sufficient to maintain a liquid phase whereby the nitrosyl chloride reacts with isobutylene and recovering butene-1 from a resulting reaction mixture.

6. A process for purifying butene-1 from its admixture with a C_4 fraction of hydrocarbon which comprises removing from said C_4 fraction a narrow boiling fraction comprising said butene-1 and isobutylene, treating said narrow boiling fraction with nitrosyl chloride in the presence of promoter quantities of water not exceeding 2 parts by weight of water per 100 parts of said narrow boiling fraction at a temperature in the range between 0 and 100° F. and under a pressure sufficient to maintain a liquid phase whereby the nitrosyl chloride reacts with isobutylene and recovering butene-1 from a resulting reaction mixture.

7. A process for purifying butene-1 from its admixture with a C_4 fraction of hydrocarbon which comprises removing from said C_4 fraction a narrow boiling fraction comprising said butene-1 and isobutylene, treating said narrow boiling fraction with nitrosyl chloride in the presence of water in an amount within the range of 1 to 2 per cent by weight of the said narrow boiling fraction at a temperature in the range

between 0 and 100° F. and under a pressure sufficient to maintain a liquid phase whereby the nitrosyl chloride reacts with isobutylene and recovering butene-1 from a resulting reaction mixture.

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REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,322,308	Moyer	June 22, 1943
2,354,359	Beckham	July 15, 1944
2,394,430	Crowder et al.	Feb. 15, 1946
2,435,570	Beckham	Feb. 10, 1948

OTHER REFERENCES

Tilden et al.: Jour. Chem. Soc., vol. 65, 334 (1894).

Tuot: Compte Rendu, vol. 204, 697–9 (1937).