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EXTRACTION OF OLEFINS

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This invention relates to a process for the separation of unsaturated hydrocarbons, and particularly olefins, from gases containing these hydrocarbons. Further, my invention relates particularly to the separation of gaseous or liquid mixtures of saturated and unsaturated hydrocarbons whose components have such slight difference in vapor pressure as to make their separation by fractional distillation difficult, if not impossible.

It is often desirable commercially to separate mixtures of paraffin and olefin hydrocarbons containing the same number of carbon atoms, or fractions containing several olefin and several paraffin hydrocarbons, the olefins having substantially the same boiling temperature range as the paraffins. The separation of such mixtures by fractional distillation is extremely difficult and often impossible because of the similarity of the vapor pressures of corresponding members of these series of hydrocarbons.

It is known to separate unsaturated hydrocarbons from gas mixtures containing these hydrocarbons by contacting the gas mixtures with various liquid absorbing agents. Examples of such liquids are liquid hydrocarbons or mixtures thereof, such as kerosene, and selective solvents which are not totally miscible with liquid hydrocarbons, such as acetone, acetaldehyde, liquid sulfur dioxide. A drawback of the use of hydrocarbons is that they are generally only slightly selective, and require a great number of stages or repeated treatments for effecting an appreciable degree of separation. Moreover, the olefins dissolve less readily in saturated liquid hydrocarbons, like those of kerosene, than the saturated hydrocarbons of the mixture being separated, necessitating a mode of operation in which the unabsorbed gas is gradually enriched with respect to the olefins.

A disadvantage of the use of selective solvents is that they have a low solvent power for olefins, necessitating the use of excessively large quantities of the extracting agent.

According to the present invention, I have found that unsaturated hydrocarbons can be more effectively separated from saturated hydrocarbon mixtures by contacting a gaseous mixture containing these hydrocarbons with a mixture of a selective solvent for olefins and a liquid hydrocarbon. In this manner the solvent power of the selective solvent is greatly increased, and the effectiveness of the separation is improved. The use of liquid hydrocarbons in combination with selective solvents often slightly reduces the selectivity of the latter, but the combined effect is such that the solubility and selectivity is more favorable than when a selective solvent is employed alone, so that the efficiency of the process as a whole is improved.

By varying the ratio of selective solvent to hydrocarbon diluent, it is possible to prepare a solvent mixture having any desired selectivity, within certain limits, combined with the most favorable solvent power. When a high degree of selectivity is not required, but it is desired to absorb a large quantity of olefins in one washing operation, the hydrocarbon content of the solvent mixture may be increased, and may often be as high as 75% by weight of the combined solvent mixture. On the other hand, when a higher degree of selectivity is desired, as little as 20% by weight of hydrocarbons may be employed.

Any selective solvent for olefins may be employed. Such a selective solvent has a greater solvent power for normally gaseous olefins than for normally gaseous saturated hydrocarbons. The following examples of suitable solvents are given without intending to limit the scope of this invention to these particular substances: nitrobenzene, benzonitrile, furfural, BB' dichloroethyl ether (Chlorex), liquid sulfur dioxide, methyl formate, acetone and alcohol.

As liquid hydrocarbons, both saturated and unsaturated aliphatic hydrocarbons boiling above the boiling temperature range of the mixture being extracted may be employed. It is also possible to employ mixtures of saturated and unsaturated liquid hydrocarbons, and petroleum fractions, such as gasoline, kerosene, and the like, and aromatic hydrocarbons, such as benzene, toluene, xylene, their homologues, and analogues. If the mutual miscibility of the selective solvent and an aliphatic hydrocarbon is insufficient, as is for example the case when furfural is used as selective solvent, which does not mix sufficiently with aromatic-free gasoline, good results are obtained by employing liquid aromatic hydrocarbons or petroleum fractions which are rich in aromatics, such as liquid sulfur dioxide-soluble gasoline extracts or kerosene extracts, such as extracts obtained by the extraction of light petroleum distillates with selective solvents of the type of sulfur dioxide. The aromatic content of such extracts may often be further increased by employing the distillate or its sulfur dioxide-soluble extract as a solvent diluent in liquid extraction processes for lubricating and similar oils, and recycling the low-boiling portion of the combined extract repeatedly.

Particularly good results are obtained by employing hydrocarbons containing one or more aromatic rings boiling below about 350° C. They may or may not contain aliphatic side chains.

The process is normally carried out at a temperature below 100° C., and at any desired pressure, such as atmospheric or superatmospheric. When treating gaseous mixtures, it is often preferable to absorb the olefins at super-atmospheric pressure, and to recover the absorbed gas by lowering the pressure, or by applying vacuum, with or without heating the fat solvent.

The gaseous mixture being treated is preferably contacted with the hydrocarbon-selective solvent mixture in a countercurrent manner, whereby the untreated mixture is first contacted with a solvent mixture rich in olefins, and the fresh solvent mixture is contacted with a mixture which has already been partly extracted. This may be effected in one or more towers arranged for the countercurrent flow of the mixture and the solvent, or in a series of mixing and settling tanks. The gas mixture is preferably caused to bubble through a body of the solvent mixture. In the case of a countercurrent tower, the solvent mixture may be introduced at the top of a tower provided with a number of perforated plates, equipped, if desired, with overflow pipes, and the gaseous mixture introduced at the bottom so as to contact successive bodies of the solvent mixture, as by flowing through the perforations and then through the body of liquid solvent mixture on the several trays.

The apparatus to be employed is well known in the art, and a further explanation thereof is unnecessary.

Example I

An excess of gaseous stabilizer reflux, containing 24% unsaturated hydrocarbons, was bubbled through 100 parts by volume of furfural at a temperature of 30° C. and a pressure of one atmosphere. The furfural dissolved 250 parts by volume of a gas containing 48% unsaturated hydrocarbons.

A further quantity of the same gas was bubbled through 100 parts by volume of a mixture of 65% by volume furfural and 35% by volume toluene, under identical conditions. The solvent mixture dissolved 440 parts by volume of a gas similarly containing 48% unsaturated hydrocarbons.

Example II

100 cc. nitrobenzene dissolved at 20° C., 500 cc. of a gaseous stabilizer reflux containing 28% unsaturated hydrocarbons. The dissolved gas contained 43 percent by volume of unsaturated hydrocarbons.

100 cc. of a mixture of 75 cc. nitrobenzene and 25 cc. aromatic-free gasoline dissolved 650 cc. of the same stabilizer reflux, the dissolved gas containing 40 percent by volume of unsaturated hydrocarbons.

I claim as my invention:

1. In a process for separating normally gaseous olefins from normally gaseous saturated hydrocarbons, the steps of bringing a normally gaseous mixture thereof in the gaseous state into contact with a liquid menstruum containing a hydrocarbon solvent and a non-hydrocarbon solvent, both being liquid under the conditions of the process, said non-hydrocarbon solvent having a greater solvent power for the said olefins than for the said saturated hydrocarbons, and separating the liquid menstruum and normally gaseous hydrocarbons in solution therein from the remainder of the normally gaseous mixture of hydrocarbons.

2. The process according to claim 1, in which the hydrocarbon solvent consists predominantly of compounds having boiling points below about 350° C.

3. The process according to claim 1 in which the hydrocarbon solvent consists predominantly of aromatic hydrocarbons.

4. The process according to claim 1 in which the hydrocarbon solvent is selected from the group consisting of benzene, toluene, and xylene.

5. The process according to claim 1, in which the hydrocarbon solvent is an SO_2-soluble extract of a low boiling petroleum distillate.

6. The process according to claim 1 in which the hydrocarbon solvent is an aromatic-free gasoline.

7. A process for adsorbing a gas rich in normally gaseous olefins from a normally gaseous mixture containing olefins and saturated aliphatic hydrocarbons, which comprises intimately contacting said mixture in the gaseous state with a liquid mixture of a hydrocarbon solvent and a non-hydrocarbon solvent, both being liquid under the conditions of the process, said non-hydrocarbon solvent having a greater solvent power for said olefins than for the said saturated hydrocarbons, separating the liquid mixture and normally gaseous hydrocarbons dissolved therein from the remainder of the normally gaseous mixture of hydrocarbons, and liberating a gas rich in normally gaseous olefins from the liquid mixture.

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