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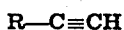
PURIFICATION OF BUTADIENE

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This invention relates to a method for purifying 1,3-butadiene and more particularly to a method for separating therefrom alpha-acetylenes which tend to distill with it and which have the general formula:



wherein R represents a lower aliphatic hydrocarbon radical, e. g., the methyl, ethyl, or vinyl radical.

In the commercial pyrolysis of hydrocarbon materials such as petroleum fractions, coal tar distillate, etc., gaseous or low boiling complex mixtures of saturated and unsaturated hydrocarbons are produced in large quantities at low cost. The mixtures thus produced often comprise the paraffin hydrocarbons ranging from methane to hexane or higher; olefines such as ethylene, propylene, butylenes, amylenes, etc.; diolefines such as butadiene, isoprene, hexadienes, etc.; and acetylenic hydrocarbons such as acetylene, methylacetylene, ethylacetylene, vinylacetylene, etc. The number and kinds of hydrocarbons in the pyrolysis mixture are dependent, of course, on the hydrocarbon materials subjected to the pyrolysis and the conditions under which the pyrolysis is carried out.

Economical methods are known whereby such complex mixtures of hydrocarbons may be separated into fractions consisting in some instances of only a single hydrocarbon and in others of only a few of the more closely related hydrocarbons in the original pyrolysis mixture, but certain of the fractions thus obtained comprise two or more hydrocarbons which are so closely related as regards certain of their physical and chemical properties that separation of the same by usual purification methods is difficult and impractical. For instance, cracked-oil gas, which often contains all of the hydrocarbons above-mentioned, may be fractionally distilled to obtain fractions consisting substantially of hydrocarbons having the same number of carbon atoms in the molecule, e. g., a fraction consisting of butane, butylenes, butadiene, ethyl acetylene, and vinyl acetylene together with minor proportions of methyl acetylene and isoprene. However, the hydrocarbons in such fraction tend to distill together and further separation by distillation is not readily attained. The acetylenes and the conjugated diolefines in particular are difficult to separate from one another. It is an object of this invention to provide a method whereby such hydrocarbons, i. e., acetylenes and conjugated diolefines, may be separated. A particular object is to provide such method

whereby the acetylenic hydrocarbons, which are usually present in smaller amounts than the diolefines, may preferentially be dissolved out of the hydrocarbon mixture with a suitable solvent.

We have discovered that when a gaseous or liquid hydrocarbon mixture comprising a conjugated diolefine and an alpha-acetylene, each having from three to five carbon atoms, inclusive, in the molecule, is brought into intimate contact with, or scrubbed by, water the alpha-acetylene is separated leaving the diolefine substantially free of alpha-acetylenes. Other hydrocarbons, e. g., olefines or paraffins, if present in the hydrocarbon mixture remain largely undissolved together with the diolefine.

The treatment of the hydrocarbon mixture with water may be carried out conveniently and in continuous manner by passing the mixture through a scrubbing tower, column, extraction chamber, or other suitable contacting chamber in counter-current relationship with water. If desired, the water may be treated previous to the extraction to free it from dissolved gases such as air and carbon dioxide to avoid introducing these substances into the extraction system. The water may also be treated to remove dissolved salts such as those of calcium and magnesium which, if present in appreciable amounts, may lead to the formation of undesirable solid deposits. The hydrocarbon mixture is preferably introduced in gaseous or vaporized form to the treatment, but it may satisfactorily be treated while in liquefied form, provided care is taken to bring the mixture into intimate contact with the water used as the extractant.

Scrubbing of the hydrocarbon mixture in the gaseous phase is usually carried out at a temperature between 0° and 150° C. and preferably between 0° and 100° C. The pressure is preferably regulated to slightly below that at which the higher boiling of the major components of the hydrocarbon mixture is liquefied at the temperature at which the treatment is carried out. The maximum solubility of the components of the gaseous hydrocarbon mixture in the water at the scrubbing temperature is thus realized and this results in treatment of a maximum amount of the mixture in any given apparatus. Lower pressures, e. g., pressure as low as atmospheric or lower, may, of course, be employed in which case the amount of hydrocarbon mixture which can be scrubbed per unit of time in a given column will be decreased and the amount of water used per unit of mixture treated will be increased. Although the optimum amount of water depends

upon a number of factors such as the composition of the hydrocarbon mixture, the dimensions of the extraction column, the pressure and temperature of the treatment and the rate of flow of the hydrocarbon mixture through the apparatus, between 100 and 500, preferably between 150 and 300, pounds of water is usually employed per pound of hydrocarbon mixture treated. The rates of flow of the gaseous hydrocarbons and of the water to the column as well as the scrubbing temperature and pressure may be regulated so as to reduce the acetylene content of the hydrocarbon gases to any desired degree. There is a very little heat effect occasioned by the contacting of the water with the gaseous hydrocarbons, and the treating temperature is usually controlled by pumping both the water and the hydrocarbon mixture to the column, while at the desired temperature.

After such gaseous phase scrubbing to remove the alpha-acetylenes, the diolefine, e. g., butadiene, is, of course, saturated with water vapor and also contains the major portion of any saturated hydrocarbons, such as propane or butane, which may be present in the hydrocarbon mixture before treatment with water. If necessary, it may be dried and further purified in known ways. The effluent water contains the alpha-acetylenes together with minor amounts of the conjugated diolefine. Unsubstituted acetylene and any minor amounts of carbon dioxide, sulfur dioxide and other water-soluble gases are also mostly removed by the treatment with water as are also smaller amounts of higher unsaturated hydrocarbons which may be present in the untreated hydrocarbon mixture.

The degree of separation of the hydrocarbon mixture may be increased by removing a part of the dissolved gases from the effluent water, e. g., by reducing the pressure or by heating, and recycling the evolved gases through the scrubbing column. Such recycled gases are rich in acetylenes as compared with the untreated mixture and are usually fed into the lower portion of the column. The water is, of course, usually fed into the top of the column and the untreated hydrocarbon mixture is usually fed into the column at an intermediate point, preferably at a point where the ascending gases in the column have approximately the same composition as the hydrocarbon feed. By recycling a portion of the water-soluble gases in the above manner, the ratio of acetylenes to conjugated diolefines in the waste water is increased considerably. If desired, the waste water may be treated further in any convenient manner for recovery of the remaining dissolved gases, e. g., methyl acetylene, ethyl acetylene, vinyl acetylene and minor amounts of 1,3-butadiene.

As hereinbefore mentioned, the hydrocarbon mixture may be treated while in liquefied form with water to extract alpha-acetylenes therefrom. Such liquid phase extraction may be carried out in suitable equipment at any pressure sufficient to liquefy the hydrocarbons and with agitation or addition of chemical dispersing agents, or other provision for obtaining rapid and intimate contact with the water. Otherwise, the extraction of the hydrocarbons in liquefied form is carried out under conditions similar to those employed in extracting the vaporized hydrocarbons with water. It is because of the inconvenience involved in effecting such intimate contact between the liquid hydrocarbon mixture and

the water that we prefer to scrub the hydrocarbons while in vaporized form.

The following example will serve to illustrate the principle of the invention, but is not to be construed as limiting its scope:

EXAMPLE

A number of experiments were carried out wherein crude gaseous 1,3-butadiene containing 85.4 per cent butadiene, 4.7 per cent of alpha-acetylenes, and 5.1 per cent higher boiling hydrocarbons was scrubbed in continuous manner with water in a column 4 inches in diameter by 30 feet long packed with Raschig rings. The butadiene was vaporized, warmed to the scrubbing temperature, and fed into the column six feet from the bottom. The water was warmed to approximately the same temperature as the butadiene and fed into the top of the column. The pressure on the column was maintained at slightly below the liquefying pressure of butadiene at the temperature of the experiment. The pressure on the effluent water was reduced to an absolute pressure of 15 to 20 inches of mercury and the gases thus recovered from the water were compressed and returned to the bottom of the column. The remaining dissolved gases, consisting largely of acetylenes together with a minor amount of butadiene were discarded with the waste water after collection of a sample for analysis. The scrubbed butadiene was collected and, while under pressure, was liquefied by cooling. The accompanying table lists the data collected during the course of the experiments. Percentages given are by weight.

Table

	Experiment No.				
	1	2	3	4	5
Crude butadiene: Lbs. treated per hour.....	1.65	2.05	1.71	3.18	3.0
Treating conditions in column:					
Temperature (°C.).....	33	34	44	55	52
Pressure (Lb. gauge).....	29	32	48	60	55
Lb. water used per hour.....	380	362	360	600	615
Purified butadiene:					
Per cent recovery.....	94	89	93	96	(¹)
Per cent alpha-acetylenes.....	0.05	0.1	0.05	0.4	0.05
Per cent high boiling hydrocarbons.....			0.9		0.9
Recycled gas:					
Per cent alpha-acetylenes.....		20	20	17	18
Lb. gas recycled per hour.....	None		1.0	1.25	1.25
Waste water: Per cent alpha-acetylenes in dissolved gas.....	78	64		61	

¹ Practically quantitative.

By a procedure similar to that illustrated in the foregoing example, isoprene may be freed from the acetylenic impurities often incident to its manufacture.

Other modes of applying the principle of the invention may be employed instead of those explained, change being made as regards the process herein disclosed, provided the step or steps stated by any of the following claims or the equivalent of such stated step or steps be employed.

We claim:

1. The method of separating alpha-acetylenes from hydrocarbon mixtures containing the same in admixture with conjugated diolefines, each having less than 6 carbon atoms in the molecule, which comprises scrubbing the hydrocarbon mixture at a temperature below 150° C. with a volume of water sufficient substantially to dissolve the alpha-acetylenes, and separating the residual hydrocarbons from the aqueous extract.

2. The method according to claim 1, in which

the scrubbing is carried out at superatmospheric pressure below that at which any of the hydrocarbons are liquefied at the temperature employed.

3. The method according to claim 1, in which the alpha-acetylenes in the mixture are from the group consisting of methyl acetylene, ethyl acetylene, and vinyl acetylene, and the conjugated diolefine is 1,3-butadiene.

4. The method of separating alpha-acetylenes from hydrocarbon mixtures containing the same in admixture with conjugated diolefines, each having less than 6 carbon atoms in the molecule, which comprises scrubbing the hydrocarbon mixture in countercurrent manner at a tempera-

ture below 150° C. with a volume of water sufficient substantially to dissolve the alpha-acetylenes, separating the residual hydrocarbons from the aqueous extract, vaporizing at least a portion of the dissolved gases from the aqueous extract and returning such gaseous portion to the scrubbing step at a point below that at which the original hydrocarbon mixture is introduced.

5. The method according to claim 4, in which the alpha-acetylenes in the mixture are from the group consisting of methyl acetylene, ethyl acetylene and vinyl acetylene, and the conjugated diolefine is 1,3-butadiene.

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