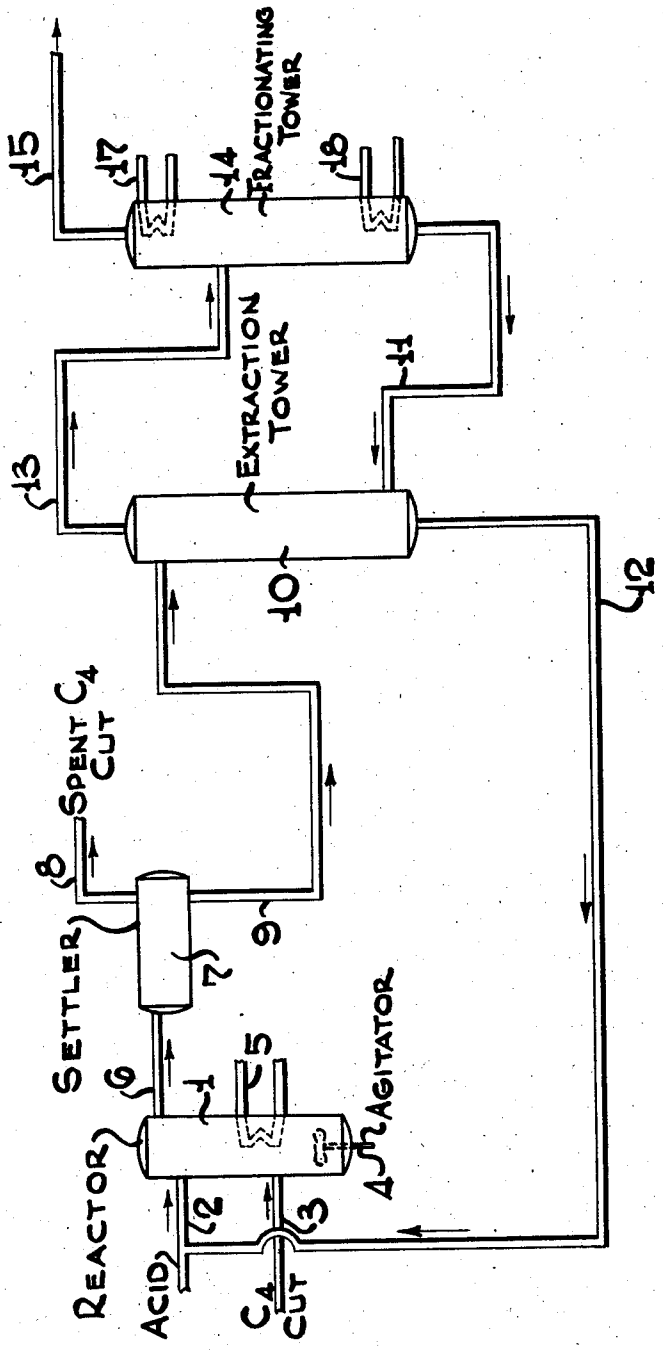
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RECOVERY OF SECONDARY OLEFINS FROM ACID EXTRACTS

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## RECOVERY OF SECONDARY OLEFINS FROM ACID EXTRACTS

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3 Claims. (Cl. 260—677)

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This invention relates to improvements in the separation and recovery of secondary olefins from mixtures of olefins and saturated hydrocarbons which are associated in gaseous and light liquid hydrocarbon mixtures and more particularly the separation of olefins having from 3 to 5 carbon atoms to the molecule from mixtures of hydrocarbons or mixtures consisting mainly of olefins and saturated hydrocarbons.

The separation of olefins by fractional distillation from saturated hydrocarbons having the same number of carbon atoms to the molecule, as in the case of mixtures produced by cracking or pyrolysis of petroleum oils or other bituminous materials, is very difficult. In most cases, it is impossible for all practical purposes, for example, to fractionally separate by distillation propylene boiling at —48.2° C. from propane which boils at —45.0° C. The separation of 4 carbon atom olefins and saturated hydrocarbons that are found in a cracked hydrocarbon mixture is still more difficult, as they are more numerous and have the following boiling points:

| | Boiling Points, ° C. |
|---|---|
| Isobutane | —10.2 |
| Isobutene | —6.6 |
| 1-butene | —6.1 |
| Butadiene | —4.75 |
| n-Butane | —0.6 |
| 2-butene, trans | —0.96 |
| 2-butene, cis | +3.73 |

The 5 carbon atom group of pentanes and pentenes is even more complex and the separation of these olefins from the associated saturated hydrocarbons by physical means has heretofore not been accomplished.

There are many chemical processes in which it is a decided advantage to use a substantially pure olefin, unmixed with inert diluents, such as saturated hydrocarbons. For example, in chemical reactions with the gaseous olefins in which pressure is advantageous, the effective pressure is normally the partial pressure of the reactive olefin in the mixture. In such cases, substantially pure olefins permit much lower pressures to be employed and less gas to be compressed than in the case of gas mixtures poor in reactive olefin. Also, in many cases the olefin reaction may be reversible, the proportion of the desired product being dependent upon the concentration of the reactive olefin in the mixture. In such cases, the dilution of the olefin with an inert diluent, such as a saturated hydrocarbon, may so affect the yield of the desired reaction

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product as to render the process unprofitable. In addition, in cases where butenes are to be subjected to pyrolysis, as in butadiene manufacture, dilution with paraffins causes (1) loss of the paraffin, which is a valuable material in itself (e. g. isobutane) and (2) difficulty in recovering the desired product after pyrolysis.

Pure olefinic hydrocarbons have been separated from naphthas containing the olefins diluted with paraffinic hydrocarbons of approximately the same boiling point by treating the naphtha with sulfuric acid under such conditions of acid strength, temperature, etc., as to selectively extract the olefins into the acid phase. The acid extract containing olefins may then be subjected to conditions whereby the olefin is recovered and the acid returned to the extraction step. This has been done heretofore by suitable dilution with water followed by steam stripping.

It is well known that sulfuric acid may readily polymerize the olefins and it is well known that, when the olefin-sulfuric acid reaction products are heated without sufficient dilution, polymerization and secondary oxidation reactions occur, such as the formation of tar or carbon, with decomposition of the sulfuric acid to sulfur dioxide and water. It is also known that under these conditions excess or uncombined sulfuric acid increases the formation of polymers. Also, the disadvantage of extract dilution and steam stripping process is in the expense involved in handling, reconcentrating and reducing the carbon content of the hot dilute slop acid.

According to the present invention the secondary olefins may be recovered from olefin-sulfuric acid solution without any substantial loss due to polymerization and secondary oxidation and without the dilution or heating of the acid extract. The following description will be related to normal butene separation but the process described will also have application to the recovery of other secondary olefins, such as propylene, normal amylene, etc.

Sulfuric acid of about 70% to 90%, preferably 83%, concentration is used to absorb the secondary olefins. This may be done at an elevated pressure in the liquid phase or at a lower pressure in the gas phase.

When normal butenes react with $H_2SO_4$, the resulting extract has been found experimentally to contain some butene as such, some as secondary butyl alcohol, and some as mono- or dibutyl sulfate. The extract is found to exert a considerable vapor pressure of normal butylene, depending on the concentration of hydrocarbon

and acid in the extract and on the temperature. Extracts of tertiary olefins, such as isobutylene, on the other hand, contain the olefin predominately as the tertiary alcohol only and exert a negligible olefin vapor pressure.

The separation and recovery of secondary olefins from strong sulfuric extracts is accomplished by the counter-current action of a saturated hydrocarbon gas having at least 20° C. difference in the boiling point from the secondary olefins such as propane or by extracting the olefins from the strong olefin-sulfuric acid extract by the counter-current action of an inert liquid solvent such as pentane or hexane. It has been found that an extract of 83% sulfuric acid containing 1 mol of olefin per mol of sulfuric acid at 30° C. is in equilibrium with a liquid naphtha containing 11% normal butene, while a similar extract containing 0.2 mol of olefin per mol of sulfuric acid is in equilibrium with a naptha containing 1.2% normal butene. Therefore the corresponding olefin vapor pressures of these two extracts are calculated to be 4.2 and 0.46 lb. per square inch, respectively. Therefore an 83% sulfuric acid extract containing 1 mol of the olefin per mol of the sulfuric acid can be stripped at 30° C. and at atmospheric pressure by passing it down a tower countercurrently through a stream of gaseous propane and the gas leaving the top of the tower should contain approximately 25% normal butene and 75% propane. The butene is then recovered by fractionation and the propane recycled. The extract leaving the bottom of the tower contains only 0.2 mol of olefin per mol of sulfuric acid and is recycled directly to the olefin absorption equipment.

Alternately, a strong extract is treated countercurrently with liquid pentane and the liquid pentane leaving at the top of the extraction tower contains approximately 10% normal butene. The butene is recovered by fractionation and the pentane recycled to the extraction tower. When some alkyl sulfate or alcohol is carried over mechanically or otherwise by the pentane, it is readily separated as bottoms in the fractionating tower and is recycled to the extraction step along with the pentane. The lean acid extract from the extraction tower is recycled directly to the olefin absorption equipment.

The stripping or the extraction process requires a suitable length of time as the reversion of alcohol or alkyl sulfate to olefins is relatively slow. Since more time is generally allowed in extraction equipment than in stripping equipment, there are certain mechanical advantages in recovering the olefin by extraction. The extraction or stripping operation may be carried out at substantially atmospheric pressure and at temperatures below that at which substantial polymerization of the olefins in the acid extract will take place, probably from 0 to 60° C.

The invention will be more clearly understood on reading the following description with reference to the accompanying drawing.

Numeral 1 designates the reactor into which is passed, at the upper part, sulfuric acid of about 83% concentration by means of pipe 2, and a mixture of hydrocarbons having four carbon atoms to the molecule and containing both butane and a secondary olefin is passed by means of pipe 3 into a lower part of the reactor. An agitator 4 is provided and cooling coil 5 to regulate the temperature. The mixture of sulfuric acid and the hydrocarbons is then passed through pipe 6 into a settler 7 where the unabsorbed hydrocarbons are removed by means of pipe 8 consisting mainly of butane. The sulfuric acid extract is removed from the settler 7 by means of pipe 9 and passed to the upper part of the liquid extraction tower 10. In the lower part of the liquid extraction tower 10 is passed a liquid paraffinic hydrocarbon solvent, such as pentane, by means of pipe 11, which passes in countercurrent flow to the sulfuric acid in the tower. The sulfuric acid, with most of the olefins removed, is then recycled by means of pipe 12 to the reactor 1. The liquid pentane with the olefin solution is removed from the extraction tower by means of pipe 13 and passed to a fractionating tower 14 where the secondary olefins are distilled over to pipe 15 and the liquid paraffinic hydrocarbon solvent is removed by means of pipe 11 and recycled to extraction tower 10. The fractionating tower 14 is provided with a condenser 17 at the upper part and a heating coil 18 at the lower part.



I claim:

1. Improvements in the separation and concentration of a secondary olefin from a hydrocarbon mixture containing the said secondary olefin which comprises contacting a hydrocarbon mixture containing a secondary olefin with sulfuric acid of about 75%–90% concentration, thereby forming a solution of the secondary olefin in said acid, extracting the secondary olefin from said acid solution by means of a saturated hydrocarbon compound, the said saturated hydrocarbon compound having at least 20° C. difference in boiling point from the secondary olefin, capable of dissolving the secondary olefin and separable from the said secondary olefin by fractionation.

2. Improvements in the separation and concentration of a secondary olefin from a hydrocarbon mixture containing the said secondary olefin which comprises contacting a hydrocarbon mixture containing a secondary olefin with sulfuric acid of about 75%–90% concentration, thereby forming a solution of the secondary olefin in said acid, extracting the secondary olefin from said acid solution by means of a saturated hydrocarbon compound in the liquid phase, the said saturated hydrocarbon compound having at least 20° C. difference in boiling point from the secondary olefin, capable of dissolving the secondary olefin and separable from the said secondary olefin by fractionation.

3. Improvements in the separation and concentration of a secondary olefin from a hydrocarbon mixture containing the said secondary olefin which comprises contacting a hydrocarbon mixture containing a secondary olefin with sulfuric acid of about 75%–90% concentration, thereby forming a solution of the secondary olefin in said acid, extracting the secondary olefin from said acid solution by means of a saturated hydrocarbon compound in the vapor phase, the said saturated hydrocarbon compound having at least 20° C. difference in boiling point from the secondary olefin, capable of dissolving the secondary olefin and separable from the said secondary olefin by fractionation.

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