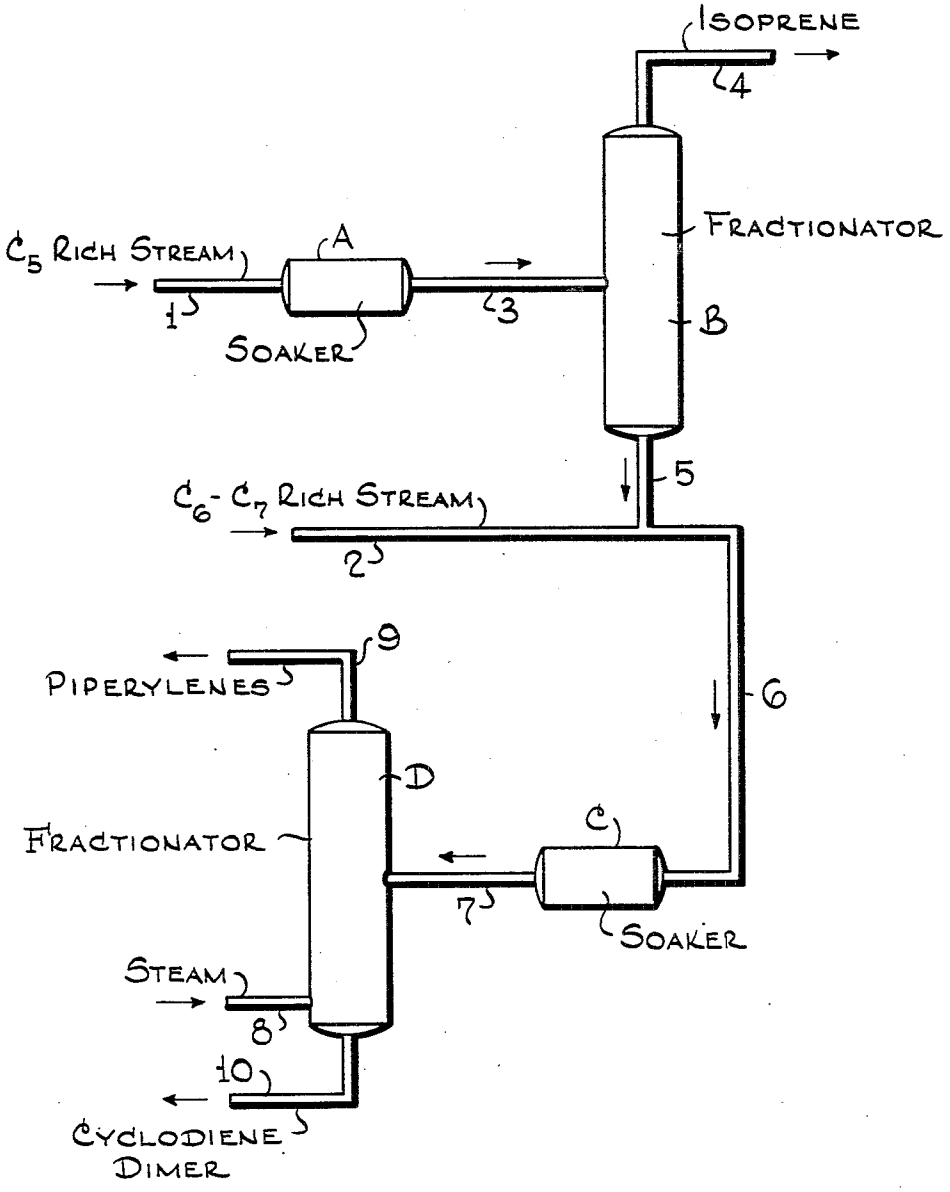
March 22, 1955 D. S. MAISEL 2,704,778

PROCESS FOR SEGREGATION OF C5 DIENES

Filed March 19, 1952



Daniel S. Maisel Inventor

By Henry Berk Attorney

United States Patent Office

2,704,778

Patented Mar. 22, 1955

2,704,778

PROCESS FOR SEGREGATION OF C_5 DIENES

Daniel S. Maisel, Union, N. J., assignor to Esso Research and Engineering Company, a corporation of Delaware

Application March 19, 1952, Serial No. 277,484

4 Claims. (Cl. 260—666)

This invention is concerned with steps developed for segregating cyclic diolefins as dimers, an isoprene-rich fraction more suitable for extraction of isoprene, and a piperylene-rich fraction.

Naphtha distillates obtained in severe cracking of petroleum oils are rich sources of valuable diolefins and aromatic hydrocarbons. The C_5+ dienes of main importance in these streams are isoprene, cyclopentadiene, piperylene, methyl cyclopentadiene, and hexadienes.

Separation of the individual diolefins, particularly isoprene, needed in high purity for synthetic rubber production, has involved difficult fractional distillation problems, even in preparing an isoprene-rich fraction for extractive distillation. This is shown in the following table:

TABLE I

Volatility relationships of C_5 hydrocarbons

Hydrocarbon Component	Wt. Percent in C_5 Fraction	Boiling Point at 25 p. s. i. g. °F.	Relative Volatility	
			Normal [1]	With Solvent [2]
Pentene-1	35.9	145	1.06	1.52
2-Methylbutene-1	7.4	147	1.03	1.47
Isoprene	14.9	153	1.00	1.00
Pentenes-2 [3]	7.4	156	0.92	1.30
n-Pentane	2.9	156	0.92	1.43
Trimethylethylene	8.4	160	0.88	1.26
Cyclopentadiene	4.9	165	0.83	0.83
Piperylene [3]	10.6	169	0.76	0.76
Cyclopentene	7.7	172	0.73	1.06
Cyclopentane	0.4	180	0.67	1.04

[1] Based on normal vapor pressures.
[2] 2 vols. solvent (92 wt. percent acetone, 8 wt. percent water) per vol. hydrocarbon in liquid phase.
[3] Cis and trans average.

By the present invention, a procedure has been developed for better recovery of isoprene, cyclopentadiene and the piperylenes with less expensive fractionation.

The basic steps in the present procedure are:

1. A light naphtha containing principally C_5 hydrocarbons, rich in isoprene, but containing cyclopentadiene and piperylenes in relatively small amounts, is easily fractionated from cracked distillates to be treated separately is used as one starting stream.

2. The light naphtha stream, rich in isoprene, is subjected to mild heat soaking for a short period to dimerize the cyclopentadiene selectively, with minimum effect on the isoprene and piperylene monomer.

3. The isoprene monomer is readily fractionally distilled from the residual part of the light naphtha stream containing cyclopentadiene dimer and the piperylenes.

4. The residual cyclopentadiene dimer concentrate from which the isoprene is distilled is suitably blended with a wider cut of C_5–C_7 or a C_6-rich stream for charging to a higher-temperature thermal soaking zone.

5. In the higher-temperature thermal soaking zone, dimerization of cyclic diolefins, including cyclopentadiene and methyl cyclopentadiene is brought to substantial completion.

6. The effluent from the higher-temperature thermal soaking zone is fractionated to distill off a distillate rich in piperylene but satisfactorily low in isoprene and cyclic diolefins.

The procedure will be described with reference to the schematic flow plan shown in the drawing.

In the flow plan, the basic feed streams used are numbered 1 and 2.

Stream No. 1 is rich in isoprene but contains substantially smaller amounts of cyclopentadiene and piperylene.

Stream No. 2 contains only a relatively small amount of isoprene but substantial amounts of piperylene, cyclopentadiene, methylcyclopentadiene, hexadiene, and benzene. Stream No. 1 is passed into heat soaking zone A for selective thermal dimerization of the cyclopentadiene but with minimum effect on the acyclic diolefins present. For this selective dimerization, the mixed hydrocarbons are heated in liquid phase under a pressure of 50–120 p. s. i. g. at 180° to about 220° F. for a period of about 4 to 12 hours. The thermal dimerization can be stopped short of complete dimerizataion of the cyclic diolefin which is principally cyclopentadiene. Preferably about 80 to 90% of the cyclopentadiene is dimerized in this first stage. This insures that the isoprene monomer is left unaffected, i. e. unpolymerized, neither dimerized nor codimerized. The effluent liquid stream from the soaking zone A is fed by line 3 into the fractional distillation tower B.

Fractional distillation tower B can be conveniently operated to take overhead by line 4 an isoprene-rich distillate satisfactorily freed of cyclopentadiene and of piperylene so that it can be readily subjected to extractive distillation by methods that are known in the art, for example, the method described in U. S. Patent 2,407,997 of J. A. Patterson. Not only can this isoprene distillate be easily fractionated to be free of cyclopentene and other C_5 aliphatic hydrocarbons higher boiling than isoprene, also, well free of cyclopentadiene and piperylene without intensive superfractionation which is expensive, since the cyclopentadiene has been largely dimerized in A.

Tower B needs only about 30 to 50 plates. It is operated under controlled conditions for keeping the piperylenes from distilling overhead with isoprene, e. g., under pressure of 15 to 30 p. s. i. g. and with a vapor overhead temperature of 130 to 150° F. Refluxing can be used in the usual manner to aid in controlling the overhead temperature.

Experimental data was found to indicate that by reducing the amount of cyclopentadiene monomer vapors in the lower part of tower B, from which the isoprene distillate is being taken overhead, separation of the isoprene from the piperylene and cyclopentene is made more readily. The cyclopentadiene monomer in a larger concentration tends to form a lower boiling azeotrope with these components.

The bottoms product of column B containing cyclopentadiene dimer and the piperylenes is maintained at temperatures sufficiently low, e. g. about 230° to 270° F. and withdrawn quickly to prevent any appreciable amount of polymerization by the piperylenes, so that the piperylenes can be subsequently recovered as monomers in the overhead from the fractionating column D, also, to prevent formation of piperylene dimer which would result in a lower purity cyclodiene dimer product and loss of the piperylenes.

The bottoms product withdrawn from tower B by line 5 should contain C_5+ hydrocarbons having normal boiling points mainly above 100° F. These bottoms should include very little isoprene, but should contain essentially the piperylenes which are to be recovered from stream No. 1.

The bottoms product of tower B withdrawn by line 5 may be added at line 6 to a broader C_5–C_7 cut or C_6 rich stream No. 2 for the further processing in the higher temperature thermal soaking zone C.

In the thermal soaking zone C, the C_5+ hydrocarbons are subjected to temperatures of 200° to 260° F. for 6 to 20 hours to insure practically complete dimerization of cyclic diolefins present. The liquid dimerization product is passed from soaker C by line 7 into an intermediate part of fractionating column D.

Column D is operated under lower pressures and at higher temperatures than first column B. Column D needs only about 20 to 30 plates. The pressure in column D is best around 5 to 20 p. s. i. g. Overhead vapors from column D should include practically all the

piperylene as monomers, that can be recovered from the types of streams indicated. The temperature of the overhead vapors from column D is maintained at a proper point for distilling overhead C_5 through C_9 hydrocarbons. At pressures of 5 to 20 p. s. i. g. the overhead vapors are maintained at a temperature of 160°–210° F. The temperature of the bottoms in column D is maintained at between 270° and 310° F. so that the bottoms product becomes a concentrated mixture of dimers and codimers formed from cyclopentadiene and methyl cyclopentadiene. This bottoms product is continuously removed by line **10**. To aid this distillation in column D, steam is injected near the bottom of column D by line **8**.

The overhead distillate product withdrawn by line **9** from column D is an excellent stream for use in recovering a maximum amount of piperylenes without hindrance by other close-boiling C_5 diolefins. This piperylene-rich stream can be subjected to a themal dimerization at temperatures of 250° to 400° F. in a period of 6 to 24 hours for recovering a large proportion of the piperylene as dimers.

If desired, this piperylene-rich stream may be subjected to other types of polymerization treatments, for example, a treatment with aluminum chloride or other catalysts to form resins. Following the dimerization or polymerization treatments, benzene present in the piperylene-rich stream can be separated.

The piperylene-rich stream may be subjected to a further fractionation to separate a narrow piperylene concentrate boiling within the range of 100°–115° F. which can be subsequently subjected to extractive distillation with various polar solvents, such as aqueous acetone, furfural, dimethyl sulfolane, etc.

The No. **1** stream rich in isoprene typically contains hydrocarbons boiling predominantly from 90° F. up to about 190° F. in using commercial fractionation. Such a stream will contain about 6 to 15 volume per cent of isoprene, if the stream is derived by high temperature cracking of naphtha to gas oil petroleum hydrocarbons. In processing these streams to obtain isoprene, it is desirable to obtain 98% purity isoprene. The cyclopentadiene and piperylene components of the same No. **1** stream are harmful impurities in isoprene. It has been demonstrated in accordance with the present invention that the separation of isoprene from these impurities is simplified by the steps of dimerizing the cyclopentadiene, then fractionally distilling the isoprene away from the residual hydrocarbons which contains the piperylene monomer mixed with the cyclopentadiene dimer.

A further benefit is obtained from the procedure outlined in allowing for a separation of the piperylene monomers from the cyclic diolefins. In prior art methods, substantial amounts of the piperylene would remain with the isoprene as contaminants which had to be removed during the extractive distillation purification of the isoprene, or the piperylene would remain with the cyclopentadiene and would undergo reaction with the cyclopentadiene.

Higher purity cyclodiene dimer products, above 90%, can be obtained by having the isoprene removed before the final dimerization treatment. At the same time, the process permits the separate isoprene and piperylene products to be recovered more efficiently.

The following data illustrates how the isoprene recovery is enhanced by lowering the cyclopentadiene monomer content in the feed to the fractionator B under comparative distillation operations.

No. 1 Feed Stream	Without Substantial Prior Dimerization	With Substantial Prior Dimerization
Isoprene Content.....wt. percent..	7.5	7.5
Cyclodiene Monomer Content.....do....	2.7	0.3
Isoprene Recovery.....percent..	67	75

It is to be understood that the examples given are not to limit the scope of the invention.

Having described the invention, it is claimed as follows:

1. A process for separating C_5 diolefins from cracked distillates which comprises heating a cracked petroleum distillate fraction rich in isoprene to a temperature in the range of 180° to 220° F. until about 80 to 90% of the cyclopentadiene present in the fraction undergoes dimerization, separating the isoprene from the thus heat-treated fraction by distillation at a temperature sufficiently low to retain piperylenes with cyclopentadiene dimer, heating the resulting cyclopentadiene dimer-piperylene containing mixture freed of isoprene in a second thermal soaking zone at 200 to 260° F., and distilling piperylene monomer from the cyclopentadiene dimer while maintaining the cyclopentadiene dimer at temperatures in the range of 270° to 310° F.

2. A process for separating C_5 diolefins from a cracked distillate naphtha fraction rich in isoprene, piperylene and cyclopentadiene, which comprises heat soaking the fraction at 180° to about 220° F. for 4 to 12 hours so that at least 80% and up to about 90% of the cyclopentadiene is dimerized, distilling an isoprene rich fraction substantially free of cyclopentadiene and free of piperylene from the heat soaked fraction, maintaining the residual heat soaked fraction containing piperylene and cyclopentadiene dimer at about 230 to 270° F. in distilling the isoprene therefrom, heating said residual heat soaked fraction freed of isoprene in a second heat soaking zone to complete selective dimerization of cyclodienes present therein so as to leave the piperylene unreacted, then distilling the piperylene from the thus dimerized cyclodienes.

3. A process for separating C_5 diolefins from a cracked distillate naphtha fraction containing isoprene with smaller amounts of piperylenes and cyclopentadiene, which comprises heat soaking said fraction to dimerize the cyclopentadiene selectively, separating isoprene from the fraction subjected to heat soaking by distilling under conditions to maintain the piperylenes in the resulting bottoms product containing the dimerized cyclopentadiene with a small amount of undimerized cyclopentadiene monomer, heating said bottoms product to dimerize the remaining cyclopentadiene present selectively, and distilling the piperylenes from the dimerized cyclopentadienes.

4. A process for separating C_5–C_6 cyclic diolefins, isoprene, and piperylene from a fraction rich in C_5 diolefin hydrocarbons and another fraction rich in C_6 diolefin hydrocarbons, which comprises mildly heat soaking said C_5-rich fraction containing the isoprene to dimerize about 80 to 90% of the cyclic diolefins present therein, fractionally distilling isoprene substantially free of piperylene from the heat soaked C_5-rich fraction to leave a residual portion containing piperylene with dimers and unreacted monomers of the cyclic diolefins, forming a mixture of said residual portion with an added fraction rich in C_6 hydrocarbons that include cyclic and acyclic olefins, heat soaking such mixture at a higher soaking temperature than used in the mild heat soaking of the C_5-rich fraction to dimerize methyl cyclopentadiene and cyclopentadiene monomers therein, then distilling piperylene from the heat soaked mixture.

References Cited in the file of this patent

UNITED STATES PATENTS

2,211,038 Ward ..... Aug. 13, 1940
2,397,580 Ward ..... Apr. 2, 1946