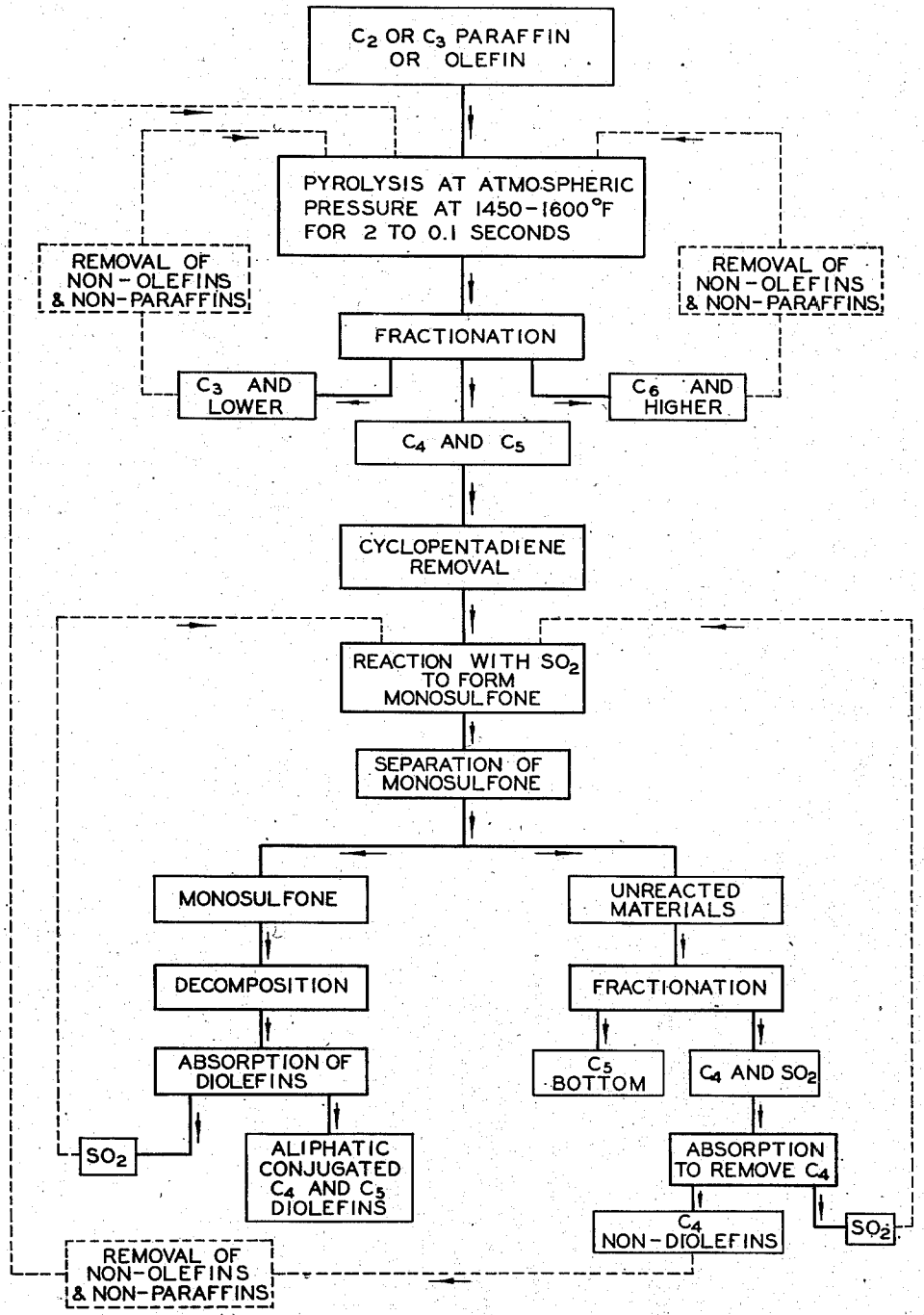
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PROCESS FOR PREPARING DIOLEFINS

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PROCESS FOR PREPARING DIOLEFINS

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3 Claims. (Cl. 260—681.5)

This invention relates to the preparation of aliphatic conjugated diolefins and more particularly to their preparation by thermal conversion of hydrocarbon material consisting essentially of a C_2 or C_3 paraffin or olefin, namely ethane, ethylene, propane, propylene and mixtures of any two or more thereof.

The principal object of the present invention is to prepare by thermal conversion aliphatic conjugated diolefins in higher yield and in higher per pass quantity than in earlier forms of the pyrolytic type of process.

A further object is to recover an aliphatic conjugated diolefin concentrate free from undesired materials and particularly undesired diolefins, from the pyrolytic reaction product in spite of the difficulties presented by the presence of a great variety of hydrocarbons in the effluent.

A still further object is to prepare a mixture consisting essentially of butadiene with non-cyclic pentadienes which has peculiar value in producing, upon polymerization, synthetic rubber having good processing characteristics.

Numerous other objects will more fully hereinafter appear.

In accordance with my invention, I subject to pyrolysis a raw feed consisting essentially of ethane, ethylene, propane, or propylene, or mixtures thereof. As raw material I prefer to use substantially pure ethylene or a C_2 material which is predominantly ethylene. I have found that even when a C_2 material predominantly or exclusively ethylene is pyrolyzed, the formation of C_5 hydrocarbon is rather marked. Whereas the C_4 hydrocarbons contained in the reaction product contain virtually no cyclic material, I have found the C_5 hydrocarbons to contain, due to reactions not thoroughly understood, a considerable amount of cyclopentadiene and cyclopentene which lowers the yield of the desired aliphatic conjugated diolefins, especially pentadienes, and renders difficult the recovery of pure aliphatic conjugated diolefin.

In accordance with my invention, the C_2 and/or C_3 paraffin or olefin hydrocarbons are pyrolyzed by heat treatment at a pressure substantially atmospheric, at a temperature of from about 1450° to about 1600° F. for a period of time of from about 2 seconds to about one-tenth of a second. With the pyrolysis thus controlled, there results an effluent containing from about one and one-half to about six weight per cent of butadiene, together with other C_4 hydrocarbons, and from about one to about two and one-half weight per cent of pentadienes, comprising a mixture of isoprene, piperylene and cyclopentadiene. The mixture usually contains some cyclopentene.

This effluent is now fractionated to separate a fraction comprising all the C_4 and C_5 hydrocarbons from lower boiling and higher boiling material. If desired, either the lower boiling, or the higher boiling material, or both, may be recycled to the initial stream for pyrolysis therewith. Recycling of the lower boiling material, where it consists essentially of C_2 and C_3 paraffins and olefins, is particularly desirable, although recycling of the higher boiling material preferably after separation of any non-paraffins and non-olefins, is perfectly feasible provided the amount recycled is not so great as to destroy the predominantly C_2 to C_3 paraffin and/or olefin nature of the feed. If desired or necessary, the lower boiling material may be treated to remove any material other than C_2 and C_3 paraffins and olefins before recycling. Acetylene, if returned, contributes to the diolefin yield. Removal of non-paraffins and non-olefins other than acetylenes and which may comprise aromatics, and other cyclic hydrocarbons from any material recycled in the process of the present invention is desirable to insure a higher yield of the desired diolefins and to prevent formation of undesirable by-products.

The C_4 and C_5 fraction thus recovered is now preferably treated to remove the cyclopentadiene content thereof in order to prevent contamination of the aliphatic conjugated diolefin product of the present invention. This may be done in a variety of ways. A preferred way is to subject the fraction in the liquid phase to thermalization in known manner to convert the cyclopentadiene content selectively to the dimer without affecting the other diolefins present. The dimer is then removed by distillation of the C_4 and C_5 fraction therefrom. More complete removal of cyclopentadiene, i. e., removal of any traces after such a treatment, may be effected, if desired, by condensation with acetone in the presence of an alkali alcoholate, such as sodium ethylate, as catalyst, followed by distillation to separate the fraction of C_4 and C_5 from the condensation product and the catalyst. Alternatively, the dimerization step may be omitted, reliance being placed on the acetone condensation procedure to remove the cyclopentadiene.

If desired, removal of cyclopentadiene may precede fractionation to recover the C_4 and C_5 material.

The C_4 and C_5 material resulting, thus freed of cyclopentadiene, is admixed with sulfur dioxide

and subjected to thermal conversion preferably under elevated pressure sufficient to maintain liquid phase and at a reaction temperature above the ceiling temperature for polysulfone formation, that is to say, under a pressure of from about 500 to about 3000 pounds per square inch and at a temperature of from about 110° to about 300° C., as disclosed in my copending application Serial No. 421,068, filed November 29, 1941.

The monosulfones of the aliphatic conjugated C_4 and C_5 diolefins are formed by the reaction with sulfur dioxide. These are separated from unreacted materials (SO_2 and non-diolefinic C_4 and C_5 hydrocarbons) in any suitable manner, it being preferred to distill off the unreacted materials from the monosulfones, thus taking advantage of the low volatility of the latter.

The monosulfones are now thermally cracked at low pressure, say about atmospheric, and at a temperature above their decomposition point, namely at least about 120° C., to regenerate the diolefins which consist of a mixture of butadiene, isoprene and piperylene, the butadiene being predominant. This mixture is particularly suitable for synthetic rubber polymerization because of the good working characteristics that it imparts to the rubber.

The products resulting from the decomposition of the monosulfones and consisting of sulfur dioxide and the diolefins are quickly cooled to a temperature sufficiently low to prevent re-reaction, and are then treated in such a way as to separate the sulfur dioxide from the diolefins as by fractional distillation or, preferably, by extraction of the diolefins with a comparatively high boiling mineral oil of low compatibility with sulfur dioxide as disclosed in my copending application Serial No. 423,535, filed December 18, 1941.

If desired the mixture of butadiene, isoprene, and piperylene thus obtained may be partially or completely resolved into its several components. Or the mixture of monosulfones may be subjected to successively more drastic thermal treatment to successively decompose the several monosulfones in the order of their thermal instability, the decomposition products being separately recovered. For example the separation of the isoprene and butadiene from the piperylene may be effected by a successively mild and drastic thermal treatment to decompose their sulfones in the order named, taking advantage of the difference in thermal stability.

The olefinic and paraffinic C_4 and C_5 hydrocarbons present in the mixture of unreacted products from which the monosulfones were removed, may be separated from unreacted sulfur dioxide and, if necessary, from any other undesirable material which may be present, such as non-paraffins and non-olefins and recycled to the initial cracking operation. The sulfur dioxide may be separated from the associated light hydrocarbons by physical extraction of the mixture with a comparatively high boiling hydrocarbon oil of low compatibility with sudfur dioxide.

I have found it to be particularly desirable, in the separation of sulfur dioxide from unreacted C_4 and C_5 hydrocarbons to subject the SO_2, C_4 and C_5 mixture to fractional distillation whereby a C_5 material essentially free from SO_2 is obtained as the kettle or bottom product, and to pass the overhead material to a vapor-liquid absorber in which the hydrocarbons are absorbed by an absorption oil, the sulfur dioxide passing out at the top. The absorbed hydrocarbon is removed from the oil by the usual stripping process.

The sulfur dioxide recovered both from the unreacted mixture left upon monosulfone separation and from the decomposition of the monosulfone is preferably recycled.

The accompanying drawing portrays a flow diagram of the process outlined above.

With regard to recycling of hydrocarbons other than C_4 and C_5 diolefins derived from the reaction effluent, and particularly of paraffins and olefins derived from the reaction effluent, it is preferred to recycle only the C_2 and C_3 paraffins and olefins in order that the feed to the cracking or pyrolysis unit may consist essentially of C_2 and/or C_3 paraffins and/or olefins. Where C_4 and higher hydrocarbons are recycled it is preferable that the amount recycled be limited so that the feed to the pyrolysis step comprises at least about 90% of C_2 and/or C_3 paraffins and/or olefins.

Following is a specific example in accordance with the present invention.

Example

Fairly pure ethylene is pyrolyzed at atmospheric pressure by passing through a tube in which it is maintained at 1475° F. for 1 second. The reaction effluent contains 4.2% of butadiene and 1.7% of pentadienes of which 0.4% is cyclopentadiene. This effluent is cooled and fractionated to separate the C_4 and C_5 material. The C_4 and C_5 fraction is then treated to remove the cyclopentadiene content by heating to 135° C. for 60 minutes, followed by distillation to separate the other C_4 and C_5 hydrocarbons from the residue comprising the dimer of cyclopentadiene.

The resulting C_4 and C_5 fraction is then admixed with sulfur dioxide in amount equal to twice the stoichiometric equivalent of the diolefin content thereof and the mixture heated at 700 pounds per square inch pressure and at a temperature of 135° C. for 3 hours. The monosulfone formed is separated from unreacted components and is subjected to heat treatment at 115° C. at atmospheric pressure to form a mixture of sulfur dioxide, butadiene, isoprene and piperylene. This mixture is quickly cooled to 30° C. and is subjected to extraction with high-boiling mineral oil to remove the diolefin content. Upon stripping the rich oil, the pure diolefins are recovered and analyze as follows:

	Per cent
Butadiene	68
Isoprene	21
Piperylene	11

It will be seen from the foregoing that the present invention provides an improved method of preparing mixed or single diolefins suitable for polymerization to synthetic rubber from readily available materials at the refinery, in a simple and economical manner.

It is to be understood that the invention is capable of numerous modifications and is not restricted to the foregoing description which is illustrative only of the preferred mode of procedure. For example, the invention may in some cases be modified so that C_6 aliphatic conjugated diolefins are prepared and are recovered along with or separately from the C_4 and C_5 aliphatic conjugated diolefins. The invention, therefore, is to be taken as limited only by the language of the appended claims.

The pressures referred to herein are gauge pressures.

I claim:

1. The process of recovering butadiene, piperylene and isoprene from the effluent of the pyrolysis of a hydrocarbon comprising predominantly an aliphatic hydrocarbon having from 2 to 3 carbon atoms at substantially atmospheric pressure, at a temperature ranging from about 1450° to about 1600° F. and for a contact time ranging from about 2 to about 0.1 second, which comprises fractionating said effluent to separate a single fraction consisting of all the C_4 and C_5 hydrocarbons contained therein, removing the cyclopentadiene content thereof by thermally dimerizing the cyclopentadiene and distilling the C_4 and C_5 fraction from the dimer, removing traces of cyclopentadiene by condensation with acetone, reacting the cyclopentadiene-free C_4 and C_5 fraction with sulfur dioxide to selectively convert substantially all of the diolefins contained therein to the monosulfone, separating the mixture of diolefin monosulfones thereby formed from the unreacted materials, and thermally decomposing said monosulfones to regenerate the butadiene, piperylene and isoprene therefrom.

2. The process of recovering butadiene, piperylene and isoprene from the effluent of the pyrolysis of a hydrocarbon comprising predominately an aliphatic hydrocarbon having from 2 to 3 carbon atoms and at least as saturated as an olefin at substantially atmospheric pressure, at a temperature ranging from about 1450° to about 1600° F. and for a contact time ranging from about 2 to about 0.1 second, which comprises fractionally distilling said effluent and thereby segregating a single fraction consisting of all the C_4 and C_5 hydrocarbons contained therein, removing the cyclopentadiene content of said fraction by thermalizing said fraction in the liquid phase to selectively convert said cyclopentadiene content to the dimer, distilling the resulting mixture to separate C_4 and C_5 fraction from said dimer, condensing traces of cyclopentadiene in the resulting distillate with acetone in the presence of an alkali alcoholate, and subjecting the resulting mixture to distillation to separate from the condensation product of said cyclopentadiene and said acetone, removing the aliphatic conjugated diolefin content of the resulting cyclopentadiene-free fraction by reacting substantially only said aliphatic conjugated diolefin content of said fraction with sulfur dioxide to form the monosulfones of butadiene, piperylene and isoprene in admixture and separating said mixture of monosulfones from the unreacted materials, and thermally decomposing said monosulfones to regenerate the butadiene, piperylene and isoprene therefrom.

3. The process of claim 1 wherein the last step thereof is conducted by subjecting said mixture of monosulfones to successively more drastic thermal treatment to decompose said monosulfones in the order of their thermal instability, and separately recovering the thus regenerated butadiene, piperylene and isoprene.

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