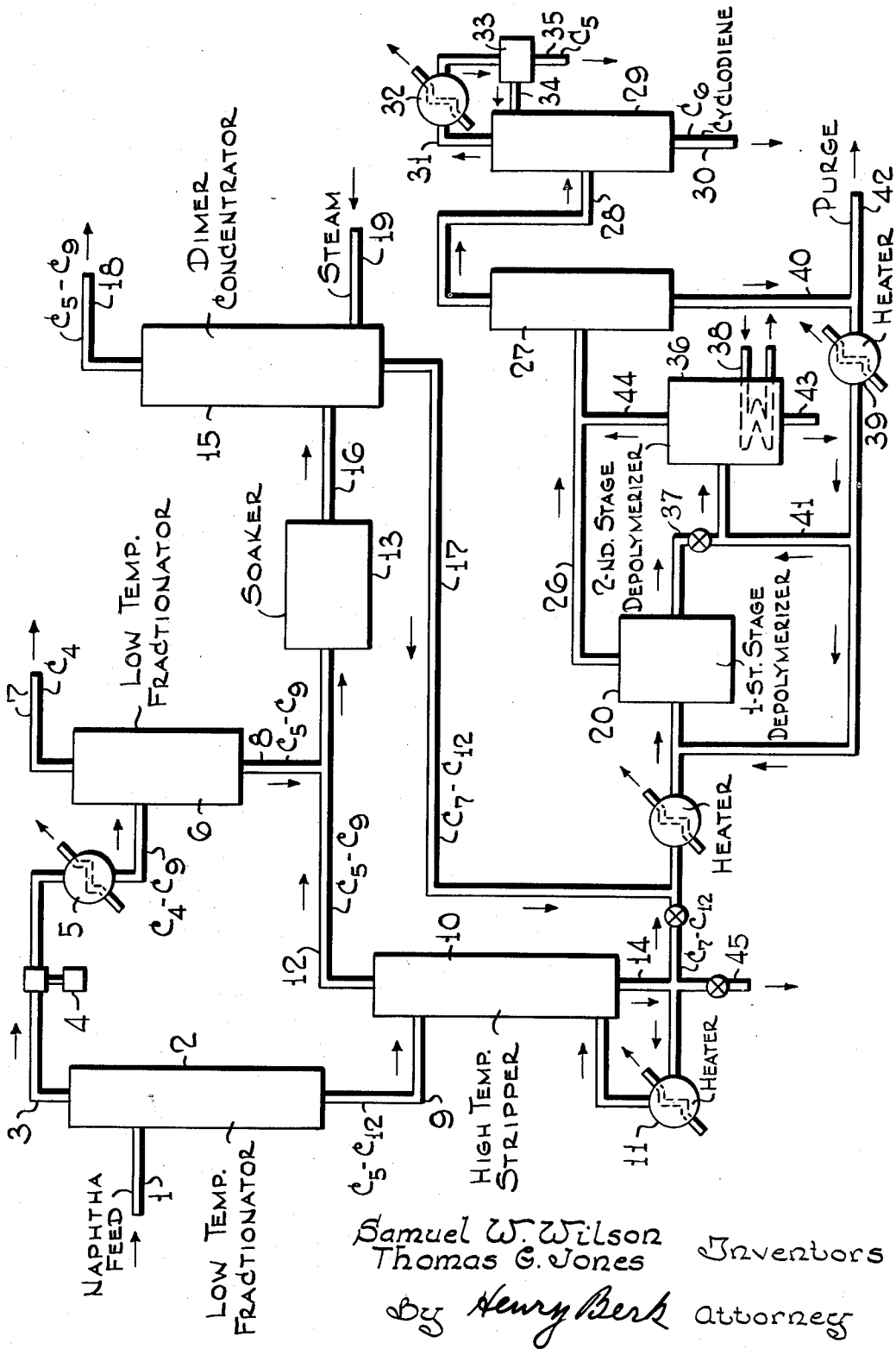
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PROCESS FOR RECOVERY AND PURIFICATION OF CYCLODIENES FROM CRACKED PETROLEUM

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Samuel W. Wilson
Thomas G. Jones Inventors

By Henry Berk Attorney

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PROCESS FOR RECOVERY AND PURIFICATION OF CYCLODIENES FROM CRACKED PETROLEUM

Samuel W. Wilson and Thomas G. Jones, Baton Rouge, La., assignors to Esso Research and Engineering Company, a corporation of Delaware

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This invention is concerned with processing of cracked petroleum hydrocarbon streams containing C_5 and C_6 cyclodienes.

An object is to isolate the cyclodienes, particularly cyclopentadiene and methyl cyclopentadiene, as monomers in effecting their purification and to recover these monomers from fractions of cracked petroleum naphtha containing the cyclodienes as monomers, dimers, and codimers mixed with other unsaturated hydrocarbons and aromatic hydrocarbons.

The present invention pertains to the following operations:

(1) An initial rough fractionation of the cracked naphtha is carried out at relatively low temperatures (e. g., below 175° F.) and with short hold-up time in obtaining a distillate fraction of C_4–C_9 hydrocarbons and a residual fraction of C_5–C_{12} hydrocarbons.

(2) Stripping of additional C_5–C_9 hydrocarbons from the residual C_5–C_{12} fraction is accomplished at relatively higher temperatures (e. g., at 240° F. to 410° F.) than the initial fractionation to insure removal of C_5–C_6 components from this residual fraction in which dimers and codimers are concentrated.

(3) Processing of the lightest fractions for eliminating C_4 and lower hydrocarbons is carried out at lower temperatures (e. g., at below 160° F.) for protection against interpolymerization.

(4) Processing of the streams of C_5–C_9 hydrocarbons to selectively dimerize the cyclodiene components and recover the resulting dimers as a residual fraction diluted with a restricted amount of C_7–C_9 hydrocarbons is carried out at moderate temperatures (e. g., at below 260° F.), preferably with the aid of steam, to minimize decomposition of the dimers.

(5) Depolymerization of C_{10}–C_{12} dimers and codimers diluted with restricted amounts of C_7–C_9 hydrocarbons in the residual streams is carried out at appropriate high temperatures mainly above 350° F. and preferably in consecutive stages at 380° to 410° F. and 390° to 420° F.

It is known that some processes have dealt only with recovery of cyclopentadiene from coal tar light ends, and others have dealt with recovery of cyclopentadiene from certain low boiling fractions of cracked petroleum distillates.

The cyclodienes present in highly cracked petroleum distillates have now been analyzed as being present in a number of homologs and polymeric forms, for example, the monomers of C_5 and C_6 cyclodienes, their higher homologs, also, the dimers, codimers, higher polymers of these homologous cyclodienes, and interpolymers with other diolefins. The dimer and codimer forms are stable at ordinary atmospheric temperatures but on being heated to elevated temperatures of the order of 280° F. and higher they start to undergo cracking or depolymerization. The monomeric forms are unstable even at ordinary temperatures and undergo polymerization as they are heated to temperatures above 140° F. On account

of the various forms in which the cyclodienes tend to be present in highly cracked naphtha distillates, there have been problems of determining the best manner of segregating a maximum amount of the cyclodienes desired and recovering them as monomers of highest purity.

In the past, the processes for the recovery of cyclopentadiene from cracked petroleum naphthas have been represented by operations which went to two somewhat opposite extremes.

In one type of prior art process, attempts were made to depolymerize all of the cyclopentadiene dimer, first in a wide boiling range naphtha including hydrocarbons lower and higher than C_5 hydrocarbons, after which the cyclopentadiene monomer together with other C_5 and lower unsaturated hydrocarbons were separated from higher hydrocarbons (C_6 and up); then the cyclopentadiene monomer was dimerized in the presence of C_5 and lighter hydrocarbons. That type of process was found unsuitable for the present objects. It omitted recovery of cyclopentadiene with methyl cyclopentadiene from their codimers, and resulted in the formation of a highly contaminated product, contamination being apparently due to the dimerization in the presence of highly reactive C_4 unsaturated hydrocarbons. The other type of process which went toward an opposite extreme for obtaining greater purity, eliminated the cyclopentadiene monomer with other C_5 and lighter hydrocarbons from the cracked naphtha distillate, so as to leave cyclopentadiene dimers highly diluted in an aromatic naphtha portion of the initial cracked naphtha and thereafter the dimer was decomposed to monomer in this aromatic fraction so that the final monomer could be fractionally distilled away from the higher boiling hydrocarbons.

The type of operation which is particularly suitable for obtaining a concentrate of the cyclodienes in accordance with the present invention is distinguished from each of the above described opposite extremes, because the present invention particularly requires obtaining a concentrate in which C_6 as well as C_5 cyclodienes are recovered to the greatest extent possible, as dimers and codimers substantially free of other hydrocarbons except for a restricted amount in the C_7 to C_9 range.

In order to obtain the cyclodiene dimer and codimer concentrates, the following division of fractions is employed:

(*a*) A light naphtha distillate cut I rich in C_5–C_6 components is readily separated from the cracked naphtha distillate if this stream is allowed to contain some C_4 components and components in the C_7 to C_9 range. This light naphtha stream is subjected to fractionation mainly at low temperatures, e. g., by compressing, cooling, and stripping to eliminate substantially all the C_4 and lighter hydrocarbons. With C_4 and lighter hydrocarbons eliminated, the remaining C_5–C_9 portion of this cut I can be soaked to dimerize said monomers, then can be fractionated at moderate temperatures to obtain a concentrate of C_{10}–C_{12} dimers and codimers with restricted amounts of C_7 to C_9 hydrocarbons.

(*b*) The heavier cracked naphtha residual fraction of C_5 to C_{12} range contains some cyclopentadiene monomer as well as methyl cyclopentadiene monomer, but it will also contain substantial amounts of the C_5 and C_6 cyclodienes in the form of C_{10}–C_{12} dimers and codimers. By subjecting this cut to fractional distillation under conditions suitable for distilling therefrom a fractional distillate principally including the C_5 and C_6 cyclodiene monomers with minor amounts of C_7 to C_9 hydrocarbons, a very good recovery is obtained from the decomposition of the dimers and codimers. This C_5–C_6 rich distillate cut is very close in its composition to the above described C_5–C_6 rich fraction from cut I with C_4 and lower elimi-

nated. Accordingly, either of the C_5–C_6 rich fractions or a combination thereof serves as a suitable feed stock for the remaining operational steps which include first a thermal soaking or dimerizing of the cyclodiene monomers present into dimers and codimers, followed by a fractionation step to remove C_5 to C_9 hydrocarbon components from the C_{10}–C_{12} cyclodiene polymers concentrate containing a minor amount of C_7 to C_9 hydrocarbons.

Next, the cyclodiene residual dimer concentrates are subjected to liquid phase depolymerization preferably in at least two stages at appropriate temperatures with rapid removal of monomers formed by decomposition of the polymers in order to minimize the reverse polymerizing reaction and assure depolymerization of the codimer.

(*c*) In a dual or multiple stage liquid-phase cracking or depolymerization, the cyclodiene dimer concentrate with controlled dilution by C_7–C_9 hydrocarbons is kept as free as possible of other types of reactive unsaturated hydrocarbon compounds and the cyclodiene polymers, mainly C_{10}–C_{12} dimers and codimers, subjected to the liquid phase cracking are prevented from being diluted excessively by hydrocarbons which would prevent the temperature from being raised to a suitable high degree. The C_5 and C_6 cyclodiene monomers that are stripped out as fast as they are formed in each of the cracking stages are immediately and quickly passed to a fractionation zone to recover distillates of the C_5 and C_6 cyclodienes having a high purity. It is essential that a limited amount of inert hydrocarbons, especially in the C_7 to C_9 range, be present to aid in stripping the monomers and for keeping the monomers diluted during their fractionation. The distillate bottoms from the fractionating zone will contain some C_5 and C_6 cyclodiene dimers and codimers with heavier polymers, but since it is desirable to prevent excessive accumulation of low boiling hydrocarbons which would prevent the desired high depolymerization temperatures from being maintained there has to be a purge of such materials. Also, a purge of higher cyclodiene polymers which resist dissociation, as the distillate bottoms are recycled to the cracking zones.

The general principles of the operations employed in the present invention have been described, and more details will be given with reference to the accompanying drawings together with specific examples.

In the drawing the general flow plan is shown for obtaining the feed stock to be used in the depolymerizing operation and final purification.

In the simplified flow plan shown in the drawing, a wide-boiling range cracked naphtha distillate stream is represented as coming from a high temperature vapor phase cracking plant through line **1**. The present invention is not particularly concerned with the method of cracking petroleum and of obtaining the naphtha distillate stream; therefore, it is sufficient to state that petroleum hydrocarbons boiling in the range of 250°–700° F. are cracked in the vapor phase at 1000° F. to 1600° F. for a short period of 1 to 5 seconds, preferably in the presence of 50 to 90 mole per cent steam based on the hydrocarbon feed and under a pressure of 1 to 10 atm. The naphtha distillate distilled from the cracked petroleum will be of approximately C_1–C_{12} range and will contain C_5 and C_6 cyclodienes in various forms, monomers, dimers, and codimers, together largely with unsaturated aliphatic hydrocarbons and aromatic hydrocarbons within this range. The naphtha distillate may be a condensed distillate which is free of the normally gaseous C_1–C_3 hydrocarbons or may be maintained in the vapor phase, including some normally gaseous hydrocarbons.

The naphtha distillate essentially containing components within the C_5–C_{12} range is passed by line **1** into what will be termed a "splitting unit," such as a conventional fractionating column **2**, for making a split between an overhead C_4–C_9 stream (cut I) and a residual C_5 to C_{12} stream (cut II). It is to be noted that this split is not made with exacting limits, and thus the overhead (cut I) stream tends to contain hydrocarbons lower than C_5 up to C_9 hydrocarbons while the residual cut II stream also contains some C_5 to C_9 components. This rough splitting between the two cuts is desirable not only for the sake of economy, but also for a number of other reasons. The rough splitting between the two cuts mentioned reduces opportunities for interpolymerization of the cyclodienes with the aliphatic diolefins and satisfactorily segregates the two types of material which are to be further processed.

Suitable operation conditions in the cut splitting operation, such as carried out in fractionating column **2**, are as follows:

No. of plates	6.
Overhead vapor temperature	60° to 100° F.
Pressures	20 to 55 p. s. i. g.
Maximum bottoms temperatures	175° F.
Holdup time of liquids below	1 to 5 minutes
Feed plate	3.

The overhead (cut I) stream removed through line **3** from the splitter unit **2** is subjected to relatively low temperature operations for eliminating C_4 and lighter hydrocarbons. These relatively low temperature operations may include compression and cooling by means of compressor **4** and heat exchanger **5** in line **3**, but finally in the fractionating column **6**, the higher boiling residual portion of the cut I stream is separated as a bottoms product substantially free of C_4 and lower boiling hydrocarbons. The eliminated C_4 and lighter hydrocarbons are removed in the overhead stream line **7** from the column **6**.

Column **6** is used purposely to remove the C_4 and lighter hydrocarbons under conditions which give very little opportunity for interpolymerization between the reactive C_4 unsaturates and the cyclodienes that are to be concentrated in the liquid residue. In general, the conditions of operation in column **6** are as follows:

Vapor overhead temperature	35° F. to 62° F.
Pressures	5 to 20 p. s. i. g.
Bottoms temperatures	135° F. to 160° F.
Holdup time below feed plate	5 to 15 minutes.

The residual bottoms are withdrawn from column **6** through line **8**. This residual bottoms portion of the cut I stream should in general have an ASTM distillation range of about 96° F. to 344° F., the high end point being due to the presence of some dimerized cyclodienes. It is interesting to note also that this residual portion of the cut I stream contains relatively small amounts of C_6 and higher hydrocarbons other than methyl cyclopentadiene and the cyclodiene dimers; for example, only about 10 weight percent of such other C_6 to C_9 hydrocarbons, including about 3 weight percent benzene. Therefore, in this residual portion of cut I, the C_5 and C_6 cyclodiene monomers are present in suitably higher concentration to undergo dimerization quite readily on being heated to a moderate soaking temperature of about 150° F. to 240° F. in a period of 12 to 6 hours.

From the splitting unit **2**, the residual cut II stream is withdrawn as bottoms through line **9** to be sent into a relatively higher temperature stripping zone **10**. The purpose of the higher temperature fractionating zone **10** is to distill over mainly a C_5–C_9 distillate which will include the C_5–C_6 cyclodiene monomers initially contained in the cut II stream and also such monomers evolved from the dimers and codimers of the cyclodienes present in the cut II stream of C_5 to C_{12} hydrocarbons. Heat is indicated to be supplied to bottoms of the fractionating zone **10** by the heater **11**. In this high temperature fractionating zone an incipient depolymerization temperature is desirable. Therefore, the holdup time can be prolonged and there is nevertheless slight opportunity for interpolymerization between the cyclodienes and ali-

phatic unsaturates since the unsaturates in the cut II stream are relatively high molecular weight and less reactive than the aliphatic unsaturates in the aforementioned cut I stream. The desired cyclodiene monomer stream is taken overhead from fractionating zone **10** by line **12**. For simplification, the cyclodiene monomer overhead stream from fractionating zone **10** is shown to be joined with the residual portion of the cut I stream withdrawn by line **8** from fractionating column **6**, thence to be subjected to a dimerization in a soaking unit **13**, although each of these streams could be separately subjected to dimerizing and later fractionation.

Typical operating conditions for obtaining the C_5 and C_6 cyclodiene monomer bearing distillate from the cut II stream of C_5 to C_{12} range, as in the high temperature stripping zone **10** are as follows:

Vapor overhead temperature	°F.	240
Pressure	p. s. i. g.	60
Bottoms temperature	°F.	410
Holdup time of liquid below feed plate—minutes		30–60

The residual liquid bottoms of the fractionating zone will contain hydrocarbons higher than C_7, including cyclodiene polymers which did not undergo decomposition.

The soaked liquid products containing substantially all the cyclodienes in the form of dimers and codimers are passed from the soaking unit **13** into a fractionating column **15** by line **16**.

The purpose of the fractionating column **15** is to separate the polymers of the cyclodienes, dimers, and codimers, as a residual bottoms concentrate that can be removed through line **17**. To obtain this concentrate, the other hydrocarbons are distilled overhead from column **15** and withdrawn through line **18** to the fullest extent possible without incurring loss of the cyclodienes by depolymerization. Therefore, column **15** is operated under such conditions that minimize depolymerization of the cyclodiene polymers while distilling therefrom the other types of C_5 through C_9 hydrocarbons that are present. In doing this, however, it has been found desirable from a practical viewpoint to leave a restricted amount of such other hydrocarbons with the polymers of the cyclopentadiene. A suitable restricted amount of such other types of hydrocarbons is of the order of 10 to 30 weight percent and mainly such hydrocarbons in the C_7 to C_9 range. Accordingly, column **15** is operated under the following represented conditions:

Number of plates		15
Overhead temperature	°F.	145
Pressure	p. s. i. g.	6
Bottoms temperatures	°F.	260
Holdup time	minutes	30

The distillation in column **15** is advantageously carried out with introduction of steam by line **19**.

The next phase of the overall operation which will be described pertains to the liquid phase depolymerization treatments and associated fractionation of the cyclopentadiene and methyl cyclopentadiene monomers that are to be recovered as a pure distillate.

The cyclodiene polymer concentrate which is withdrawn as bottoms from column **15** through line **17** is sent to a first stage of the first cracking or depolymerizing vessel **20**. Residual liquid from the high temperature stripper is sufficiently free of cyclodiene dimers and may be removed by line **45**.

Vapors evolved from the liquid polymer concentrate in vessel **20** are to be rapidly withdrawn therefrom. The liquid polymer concentrate in vessel **20** has to be maintained at a sufficiently elevated temperature, above 350° F., for accomplishing the depolymerization while the liquid is boiling under a pressure that maintains the cyclodiene polymers in liquid phase, e. g., a moderate pressure of 2 to 20 p. s. i. g. Increased pressures favor the repolymerization of cyclodiene monomers and are, therefore, to be avoided. Accordingly, the vapors taken overhead from vessel **20** should principally comprise the C_5 and C_6 cyclodiene monomers with a minor volume proportion of C_7–C_9 hydrocarbons that beneficially act as diluents and stripping agents.

The vapors taken overhead from vessel **20** may be passed up through a superimposed refluxing zone but they should be passed quickly by line **26** to the fractionating column **27**. Practically all the C_5 and C_6 cyclodiene monomer vapors are to be carried rapidly with C_7 to C_9 hydrocarbon vapors to the fractionating column **27**.

In fractionating column **27**, the vapors from line **26** undergo fractionation on passing upwardly through 5 to 10 plates at temperatures of the order of 175° F. to 160° F. In this fractionation, C_7 to C_9 hydrocarbons with a small amount of cyclodiene dimers formed through repolymerization are condensed to liquid which flows to the bottom of column **27**. The C_5 and C_6 cyclodiene monomers in purified form reach the upper plates of fractionating column **27** at temperatures of 150° to 160° F. and then may be distilled overhead for further fractionation, or a mixed monomer distillate may be condensed and collected.

Overhead distillate from fractionator **27** may be passed by line **28** into a subsequent fractionator **29**, wherein the C_6 cyclodiene is condensed and recovered as a bottoms fraction withdrawn by line **30**. The cyclopentadiene or C_5 cyclodiene monomer vapor is recovered as a distillate as it is passed through overhead line **31**, then through cooling condenser **32** and collected in receiver **33**. Some refluxing of cyclopentadiene distillate from receiver **33** through line **34** to the upper part of fractionator **29** is helpful in making a sharper separation between the individual monomer products. The cyclodiene product is removed by line **35**.

The fractionator **29** is operated at temperatures between a bottoms temperature of about 160° F. and a top temperature of about 120° F.

The second stage depolymerizing vessel **36** receives residual cyclodiene polymer liquid from vessel **20** through line **37** and is advantageously operated at a higher depolymerization temperature. Heat may be supplied to vessel **36** by suitable heating means, e. g. heating coil **38** and a heat exchanger **39** for supplying heat to recycled bottoms condensate from fractionator **27** as this concentrate is returned through line **40** and line **41** to vessel **36**.

Control of the liquid recycle from the bottom of fractionator **27** to either vessel **20** or **36**, or to both, is necessary to prevent accumulation of relatively low-boiling C_7 to C_9 hydrocarbons in these vessels. Therefore, to avoid excessive buildup of these relatively lower-boiling hydrocarbons, some of the reflux being recycled through line **40** is purged through a withdrawal line **42** or withdrawal line **43** from vessel **36**. The cyclodiene monomer vapors are withdrawn overhead as rapidly as possible from vessel **36** and may be passed directly by line **44** to join the stream of vapors in line **26** entering the fractionator **27**. The vapors leave the vessel **36** at a temperature of about 350° F. to 380° F.

The following factors guide the selection of operating conditions during the depolymerizing treatment of the cyclodiene polymer concentrates:

(*a*) The depolymerization of the polymer concentrates is negligible until the temperature of the liquid concentrate is maintained at above 350° F.

(*b*) The cyclodiene monomers have to be stripped from the liquid concentrate as fast as they are formed with the aid of a limited amount of C_7 to C_9 hydrocarbons since excessive amounts of these intermediate boiling hydrocarbons would lower the temperature in the depolymerization zone.

(*c*) After a substantial amount of the cyclodiene dimers undergo depolymerization in the concentrate, it is necessary to increase the depolymerization temperature, e. g. to above 380° F., to accomplish further depolymerization at a suitable rate.

(*d*) The monomer bearing vapors being transferred from the depolymerization zones to a fractionation zone have to be substantially free of other close-boiling hydrocarbons, especially other C_5–C_7 hydrocarbons boiling up to about 175° F., so that the separation of these monomers by fractionation can be carried out most expeditiously with quick cooling in order to avoid recombination of the monomers into dimers and higher polymers that have greater thermal stability than the dimers and make this recovery of the available cyclodienes.

Summarized results of continuous two-stage liquid phase depolymerization runs on cyclodiene polymer concentrates are given in the following tabulation:

TABLE

Continuous two-stage operation

FEED: Concentrate of 67.7 weight per cent dimerized cyclodienes with C_7–C_9 hydrocarbons.
CONDITIONS: Feed charged continuously to two-stage unit for 8–10 hours total residence time. Vapors were removed from each depolymerizing vessel continuously to 5th plate of a 20 plate Oldershaw column held at 160° F. overhead temperature. Bottoms of column were recycled to first stage. Purge was taken from second stage to hold unit in balance.

Total Run Length, Hrs.	Depolymerization Temp., ° F.		Recovered Product		
	1st stage	2nd stage	Wt. Percent Yield of Monomers on Crude Feed	Purity, Wt. Percent	Recovery, Wt. Percent, Based on Available Cyclodiene
12	350	350	0		
13	380	390	59.3	92.2	75.2
14	390	400	56.8	93.2	85.9
14	400	410	57.7	96.1	89.5
13	410	420	64.6	89.2	93.4

The data of the table showed quite emphatically that the temperature required for satisfactory recovery and high purity are substantially above 350° F., preferably in the range of 380° to 410° F. and 390° to 420° F. for the second stage.

The feed used in making the runs shown in the table was a concentrate obtained by first combining a C_5–C_6 light cracked naphtha fraction with a C_5–C_9 cracked naphtha fraction, dimerizing the combined fractions at 240° F. for 6½ hours, then fractionating to remove mostly light C_7 and lower boiling hydrocarbons from the residual concentrate. The operation rate tolerated recycling up to 18 weight % of the cracker product fractionator bottoms from column 27 based on the fresh feed.

Reviewing features of the process described in comparison to other types of processes, the advantages of the presently developed process were determined to be considerable with regard to higher recovery of the monomers with high purity at lower investment cost.

The added amount of cyclodiene polymer in the concentrate from the separately treated low-boiling distillates (of C_5–C_9 range) gave a 50% increase in yield of recovered cyclodiene monomers. This increase in yield is accounted for particularly by recovery of cyclopentadiene with methyl cyclopentadiene from a large part of their monomers and polymers and partly by repression of interpolymerization of the cyclodienes with the reactive dienes present in the low boiling C_4 to C_9 streams handled at low temperatures.

The stage-wise cracking of the concentrated cyclodiene polymers at elevated temperatures above 350° F. in the presence of limited amounts of C_7 to C_9 hydrocarbons permitted maintenance of the elevated temperatures in the depolymerization and reduced the purging, thus making a saving in depolymerizing and fractionating equipment and thus lowering the loss of polymers in the purge. In the stage-wise cracking, the temperature maintained in any stage may be between 350° F. and 450° F., but the temperature should be at least above 380° F. in one stage to obtain efficient depolymerization.

Having described the invention it is claimed as follows:

1. In receovering C_5 and C_6 cyclodienes from cracked petroleum naphtha, the steps which comprise distilling from the naphtha a C_4 to C_9 hydrocarbon cut at temperatures below 175° F., removing C_4 hydrocarbons from the C_4 to C_9 cut at temperatures below 160° F to obtain a remaining C_5 to C_9 hydrocarbon fraction, soaking said C_5 to C_9 hydrocarbon fraction at temperatures of about 150° F. to 240° F. until the cylodienes in said fraction are dimerized, fractionally distilling C_5 to C_9 components from the resulting soaked fraction to obtain the cyclodiene dimers as a concentrate substantially free of C_6 and lower-boiling hydrocarbons, passing a high boiling residual portion of said initial cracked naphtha containing C_5 to C_{12} hydrocarbons into a high temperature stripping zone, stripping said residual naphtha fraction of additional C_5 to C_9 hydrocarbons at temperatures between 240° F. and 410° F., soaking said additional C_5 to C_9 hydrocarbons at about 150° F. to 240° F. to obtain more of the cyclodiene dimers, passing the cyclodiene dimers into a depolymerization zone in which the cyclodiene dimers undergo depolymerization at temperatures ranging from above 350° F. to about 450° F., rapidly removing the resulting cyclodiene monomer vapors with higher boiling C_7–C_9 hydrocarbons present in said concentrates to a fractionation zone, and fractionally separating the cyclodiene monomers.

2. In recovering C_5 and C_6 cylodienes from cracked petroleum naphtha, the steps which comprise fractionally distilling from the naphtha a distillate fraction of C_4 to C_9 hydrocarbons at below 175° F. to obtain a residual fraction of C_5 to C_{12} hydrocarbons, stripping from said residual fraction at temperatures in the range of 240° F. to 410° F. a C_5 to C_9 distillate fraction containing C_5 and C_6 cyclodienes with some higher components in the C_7 to C_9 range but free of hydrocarbons lower boiling than the cyclodienes, dimerizing the C_5 and C_6 cyclodiene monomers present in said C_5 to C_9 fraction, concentrating resulting C_{10} to C_{12} cyclodiene dimers and codimers formed in the C_5 to C_9 fraction and stripping therefrom C_5 to C_9 hydrocarbons until the resulting residual concentrate contains 60 to 90% of said dimers and codimers with less than 40% of hydrocarbons in the C_7 to C_9 range.

3. In recovering C_5 and C_6 cylodienes from cracked petroleum naphtha, the steps which comprise fractionally distilling at below 175° F. C_4 to C_9 distillation fraction from the naphtha to form a residual C_5 to C_{12} fraction, stripping additional C_5 to C_9 hydrocarbons from said residual C_5 to C_{12} fraction at 240° to 410° F., stripping C_4 and lower hydrocarbons from said C_4 to C_9 distillate fraction at below 160° F. to form a second residual C_5 to C_9 fraction, combining said residual C_5 to C_9 fractions, dimerizing C_5 and C_6 cyclodiene monomers present in said combined C_5 to C_9 fractions, concentrating resulting C_{10} to C_{12} cyclodiene dimers and codimers formed in said combined C_5 to C_9 fractions by stripping therefrom C_5 to C_9 hydrocarbons until a residue of said combined fractions contains 60 to 90% of the C_{10} to C_{12} cyclodiene dimers and codimers with less than 40% of hydrocarbons in the C_7 to C_9 range.

4. In the process defined by claim 3, depolymerizing the C_{10} to C_{12} dimers and codimers in said resulting residual concentrate at temperatures in the range of 380° F. to 420° F.

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