

[54] **PROCESS FOR THE PRODUCTION OF CYCLOPENTADIENE FROM DICYCLOPENTADIENE**

[75] Inventors: **Fritz Grude; Kurt Halcour**, both of Leverkusen; **Wulf Schwerdtel**, Cologne; **Wolfgang Swodenk**, Odenthal-Globusch; **Peter Woernle**, Leverkusen, all of Germany

[73] Assignee: **Farbenfabriken Bayer Aktiengesellschaft**, Leverkusen, Germany

[22] Filed: **April 20, 1971**

[21] Appl. No.: **135,694**

[30] **Foreign Application Priority Data**

April 23, 1970 Germany.....P 20 19 596.4

[52] U.S. Cl.260/666 A

[51] Int. Cl.C07c 13/14

[56] **References Cited**

UNITED STATES PATENTS

2,636,054 4/1953 Johnson.....260/666 A

2,508,922 5/1950 Luten et al.260/666 A
 2,831,904 4/1958 Kreps260/666 A
 3,007,978 11/1961 Beach.....260/666 A
 3,544,644 12/1970 Robota260/666 A

Primary Examiner—James E. Poer
Assistant Examiner—A. P. Demers
Attorney—Burgess, Dinklage & Sprung

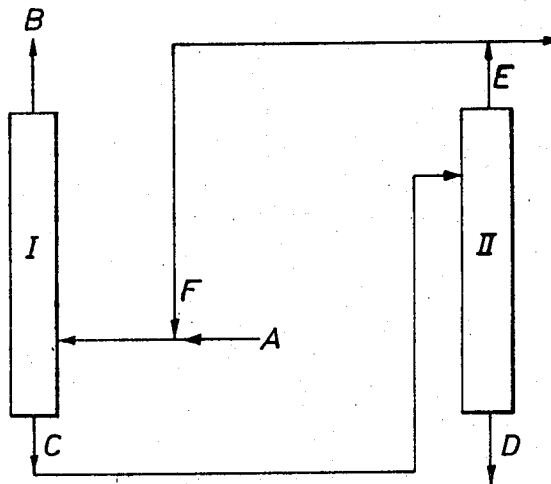
[57] **ABSTRACT**

The process for the production of cyclopentadiene by the substantially quantitative splitting or monomerizing of a dicyclopentadiene concentrate containing thermally stable dimers of isoprene and codimers of cyclopentadiene, isoprene and piperylene and having been obtained by the heat treatment of a C₅ fraction of a pyrolysis petrol and its subsequent enrichment by fractional distillation, comprising heating the dicyclopentadiene concentrate in liquid phase in a reactor at a temperature of about 170° to 250° C., and maintaining a concentration of about 10 to 70 percent by weight for the thermally stable dimers of isoprene and codimers of cyclopentadiene, isoprene and piperylene in the reactor.

8 Claims, 1 Drawing Figure

PATENTED MAR 6 1973

3,719,718



INVENTORS:

FRITZ GRUDE, KURT HALCOUR, WULF SCHWERDTL, WOLFGANG SWODENK, PETER WOERNLE.

BY

**PROCESS FOR THE PRODUCTION OF
CYCLOPENTADIENE FROM
DICYCLOPENTADIENE**

This invention relates to the substantially quantitative production of cyclopentadiene from a fraction rich in dicyclopentadiene, which has been obtained by subjecting a C₅ pyrolysis petrol to heat treatment and fractionation, by thermally splitting in the liquid phase the dicyclopentadiene present in this fraction.

In the pyrolysis of petroleum fractions for the production of ethylene a C₅+fraction is obtained in addition to a C₃ fraction and a C₄ fraction so-called "pyrolysis petrol." The C₅+fraction of the pyrolysis petrol contains inter alia isoprene, cyclopentadiene and piperylene. In a further treatment of this C₅ fraction, the cyclopentadiene is usually dimerized into dicyclopentadiene before the C₅ fraction is subjected to further working up. In this way, it is possible to separate the C₅ fraction by distillation into a fraction containing isoprene and piperylene, and a much higher boiling dicyclopentadiene fraction. The two fractions can then be separately worked up; for example, the C₅ fraction containing isoprene and piperylene can be worked up into isoprene and the dicyclopentadiene fraction can be worked up into monomeric cyclopentadiene.

So far as further working up of the dicyclopentadiene is concerned, proposals have been made to split dicyclopentadiene into cyclopentadiene in the gas phase (cf. U.S. Pat. Nos. 2,409,259; 2,733,280; 2,733,283; 2,913,504, 2,994,724, 3,007,978; 2,511,936 and 2,582,920, and British Pat. Specifications Nos. 573,592; 1,018,046 and 807,800).

The disadvantages of gas-phase splitting include the remarkably high consumption of energy attributable to the high temperature required for splitting, and the risk of reactor coking which the high reaction temperatures involve. To prevent coking, conventional industrial processes are carried out in the presence of inert diluents, for example inert gases or steam, but these only further increase the energy costs and complicate the working up of the reaction products (cf. U.S. Pat. Nos. 2,453,044; 2,801,270 and 2,508,922 and Hungarian Pat. Specification No. 151,720).

In addition, it has been suggested some time ago that dicyclopentadiene can be monomerized in the liquid phase with long residence times. Unfortunately, this process results in the formation of polymers of cyclopentadiene which causes clogging of the apparatus over a period of time (cf. N.F. Kononov, *Isvest. Akad. Nauk. U.S.S.R., Ser. Khim* 1953, 112-113; C.A. 48, 10377e and 13273d).

One way of avoiding these difficulties encountered in the monomerization of dicyclopentadiene in the liquid phase is to effect only partial reaction of the dicyclopentadiene, in which case a considerable proportion of unreacted dicyclopentadiene has to be removed from the process together with the cyclopentadiene polymers.

Proposals have also been made that the dicyclopentadiene formed through dimerization during further working up of the cyclopentadiene by distillation should be recycled to the reaction. (cf. U.S. Pat. Nos. 2,636,056; 2,733,279; 2,735,875; 2,751,422; 2,753,326 and 2,813,134, British Pat. Specifications Nos. 635,910; 759,327 and 775,113, Dutch Pat.

Specification No. 91,149 and *Oil and Gas Journal*, Jan. 15, 1962, page 109). This expedient does not permanently prevent resinification of the apparatus used for the splitting process.

Accordingly, it has been proposed to use auxiliary liquids for the splitting process in the liquid phase in order to prevent resinification and the consequent substantial losses of starting material. This procedure is described in numerous patent specifications. British Pat. Specification No. 771,650 describes the addition of organic solvents which boil at temperatures above 250° C. and which do not show any solubility for dicyclopentadiene. British Pat. Specification No. 769,813 describes the addition of different organic solvents into which the dicyclopentadiene is introduced in vapor form. U.S. Pat. No. 2,887,517 describes the splitting of dicyclopentadiene in the presence of three times the volume of higher paraffin hydrocarbons. British Pat. Specification No. 612,893 describes the addition of gas oil as an auxiliary liquid. U.S. Pat. Nos. 2,387,993; 2,636,054 and 3,016,410 describe the splitting of dicyclopentadiene at very low concentrations.

In order to eliminate the difficulties affecting the splitting of dicyclopentadiene, it has further been proposed to add inert gases, such as steam for example, in addition to a foreign solvent (U.S. Pat. No. 2,453,044).

It is accordingly an object of the invention to provide a liquid phase process for converting dicyclopentadiene to cyclopentadiene which does not require excessive heating or additional liquids or result in clogging of the apparatus after short runs.

These and other objects and advantages have been realized in accordance with the present invention wherein there is provided a process for the production of cyclopentadiene by the substantially quantitative splitting or monomerizing of a dicyclopentadiene concentrate containing thermally stable dimers of isoprene and codimers of cyclopentadiene, isoprene and piperylene and having been obtained by the heat treatment of a C₅ fraction of a pyrolysis petrol and its subsequent enrichment by fractional distillation, comprising heating the dicyclopentadiene concentrate in liquid phase in a reactor at a temperature of about 170° to 250° C., and maintaining a concentration of about 10 to 70 percent by weight for the thermally stable dimers of isoprene and codimers of cyclopentadiene, isoprene and piperylene in the reactor. The pressure may be about normal or slightly elevated, e.g., up to about 1.5 at (7 psig) or more.

In one particularly advantageous embodiment of the process according to the invention, a concentration of up to 50 percent is maintained for the polymer fraction in the sump of the splitting apparatus. To this end a portion of the bottom product in the reactor is continuously withdrawn and subjected to distillation, preferably using a thin-film evaporator, the thermally stable dimers and codimers coming off as distillate being recycled at least in part to the reactor.

In this way, the dicyclopentadiene can be dissociated in an amount of more than 90 percent. A residence time of less than about 5 hours is best maintained for the splitting reaction coupled with the highest possible heat transferred per unit surface.

The advantage of the process according to the invention over a procedure of the kind adopted in conventional processes is that it is now possible, in cases where a highly concentrated dicyclopentadiene obtained from a heat-treated C_5 fraction of a pyrolysis gasoline is used, to carry out splitting into monomeric cyclopentadiene substantially quantitatively without any need to add a foreign auxiliary liquid and with little or no need to recycle the dicyclopentadiene, thus eliminating the risk of resinification in the splitting apparatus. It must be regarded as particularly surprising that no resinification occurs where a concentration of from 10 to 70 percent is maintained in the bottoms product of the splitting apparatus for the codimers and dimers of cyclopentadiene, isoprene and piperylene. Resinification is not prevented where unreacted dicyclopentadiene is used as a diluent for the resins formed, as suggested in a number of Patent Specifications to which references has already been made.

BRIEF DESCRIPTION OF DRAWING

The accompanying drawing shows a flow diagram in which dicyclopentadiene (A) obtained by dimerization of cyclopentadiene, followed by fractionation is fed into a distillation column I. Crude Cyclopentane (B) is withdrawn overhead, Bottoms product (C) is delivered to a thin-film evaporator (11). Resin (D) is obtained as the sump product of the thin-film evaporator (11). Distillate (E) is removed overhead and a portion thereof (F) is pumped with starting dicyclopentadiene into column (I).

In general, the process according to the invention is carried out as follows:

Monomerizing can be effected either at normal pressure or under a slight excess pressure in a distillation apparatus comprising an evaporator, preferably a thermosiphon evaporator, a separator, a fractionating column with a few plates, preferably two to 10 plates, and a dephlegmator or condenser with a reflux pump. The product to be split or monomerized containing more than about 70 percent by weight of dicyclopentadiene, which originates from the fractional distillation of dicyclopentadiene-containing C_5 cuts of a pyrolysis petrol, and the recycled codimers described below are continuously pumped into the sump or into the fractionating column. In addition to dicyclopentadiene, the starting material contains the other C_{10} hydrocarbons known as codimers and dimers, and optionally remaining amounts of C_5 hydrocarbons. Accordingly, the sump product of the monomerization apparatus comprises dicyclopentadiene, thermally stable codimers of cyclopentadiene with isoprene and of cyclopentadiene with piperylene, dimers of isoprene and the cyclopentadiene polymers accumulating during splitting. The sump product is heated to boiling point (170° to 200° C.), advantageously in thermosiphon or forced-circulation evaporators. In order to increase the yield, the residence time should be as short as possible, preferably less than 5 hours, and the heat transferred per unit surface should be as high as possible. The sump level of the monomerization apparatus is kept constant by running off sump product either continuously or at intervals. The throughput of dicyclopentadiene to be monomerized is so high that most of the dicyclopentadiene is immediately converted to cyclopentadiene.

The sump boiling under reflux promotes development in the fractionating column of a temperature and concentration profile which can be influenced by the dicyclopentadiene input, by recycling of the codimers, by the heat transferred per unit surface and also by the reflux ratio. The conditions have to be selected in accordance with the purity in which the cyclopentadiene is required. The cyclopentadiene obtained preferably contains less than 2 percent by weight of dicyclopentadiene and codimers. In cases where a dephlegmator is used, the cyclopentadiene obtained can be used directly, i.e., without condensation, for subsequent processes, for example, hydrogenation. If it is desired to obtain the cyclopentadiene in liquid form, it has to be cooled after condensation to temperatures below -20° C. (because it is quickly dimerized again at temperatures higher than this), after which it can be further treated.

In the process described above, the overall conversion amounts to between 90 percent and 95 percent, based on the dicyclopentadiene used, and resin formation amounts to between 5 percent and 10 percent by weight. In addition to at the most 2 percent by weight of C_{10} hydrocarbons, mainly dicyclopentadiene, the cyclopentadiene only contains the volatile C_5 compounds which were already present in the starting material.

In view of the concentration figures according to the invention, it is best to run off preferably 5 to 40 percent of bottoms product, based on the dicyclopentadiene used, from the sump of the monomerization or splitting apparatus, followed by working up preferably in a thin-film evaporator. A distillate most of which consists of the codimers and which can be completely or partly recycled into the monomerization apparatus, is run off in the thin-film evaporator at a temperature of about 180° to 250° C.

Accordingly, it is possible by virtue of the process according to the invention largely to monomerize dicyclopentadiene in the liquid phase in the absence of any auxiliary liquids. This eliminates the costs which these auxiliary liquids would otherwise entail and avoids the difficulties involved in quantitatively removing foreign substances from the end product which is usually necessary for further processing purposes.

The invention is further illustrated in the following example wherein all parts are by weight.

EXAMPLE

1,500 g per hour of an 82 percent dicyclopentadiene obtained by dimerization of the cyclopentadiene present in a C_5 pyrolysis petrol fraction, followed by fractionation, were pumped continuously into the sump (8 liters) of distillation column, (I). The cured dicyclopentadiene contained the codimers of cyclopentadiene with isoprene and piperylene formed during dimerization as well as dimers of isoprene.

Analysis:	dicyclopentadiene	82.0% by weight
	codimers and dimers	13.0% by weight
	C_5 hydrocarbons	5.0% by weight

100.0% by weight

The sump was heated to boiling point (170° to 180°C) under atmospheric pressure by natural circulation in a steam-heated thermosiphon evaporator. The boiling constituents and the cyclopentadiene formed through monomerizing of the dicyclopentadiene were rectified in a 3.50 meters long, 50 mm wide fractionating column packed with 10 mm fillings arranged on the evaporator. A temperature profile of between 180° C. and 50° C. was developed in the fractionating column. The concentration of the dicyclopentadiene fell from 20 percent by weight at the lower end to around 2 percent by weight at the upper end of the fractionating column. A dephlegmator run on water heated to around 50° C. was arranged on the fractionating column. 1,205 g/hour of distillate containing 92.9 percent of cyclopentadiene were obtained downstream of the dephlegmator.

Analysis:	cyclopentadiene	92.9 %
	other C ₅ hydrocarbons	6.2 %
	C ₁₀ hydrocarbons	0.8 %
		99.9 %

The yield came to 91 percent, based on the dicyclopentadiene used.

In order to maintain the level of the sump in the distillation unit, a certain quantity of bottoms product was initially run off. This bottoms product was pumped into a thin-film evaporator (II) operated at 225° C. wall temperature. A thixotropic sump product of pasty consistency was run off from the lower end of the thin-film evaporator.

The distillate was added to the starting dicyclopentadiene and thus re-entered the sump of the cracking apparatus. An equilibrium was formed after a short time. Of the 1,500 g per hour of 82 percent dicyclopentadiene used (A), 1,205 g/hour were run off downstream of the dephlegmator; this product contained 1,120 g of cyclopentadiene (92.9 percent by weight), 75 g of C₅ hydrocarbons (6.2 percent by weight) and 10 g of C₁₀ hydrocarbons (0.8 percent by weight) (B). In this case, the cyclopentadiene yield amounted to 91 percent. It amounted to between 90 percent and 95 percent during a long-term test.

After the equilibrium had been adjusted, 395 g/h of bottoms product (C) were run off from the sump of the monomerization apparatus and delivered into the thin-film evaporator operated at 225° C. 80 g/hour of resin (D) were obtained as the sump product from the thin-film evaporator, together with 215 g/h of distillate (E) which consisted of 20 g of dicyclopentadiene (9.3 percent by weight) and 195 g of thermally stable codimers and dimers (90.7 percent by weight). 110 g/hour of this distillate (F) were pumped with the starting dicyclopentadiene into the monomerization apparatus

so that the proportion of thermally stable compound in the monomerization reactor was kept at around 70 percent. The proportion of polymers in the reactor amounted to 22 percent. Under these conditions, it was possible to continue the dissociation of dicyclopentadiene for a period of 1,500 hours with a cyclopentadiene yield of 90 to 95 percent, based on the dicyclopentadiene used. The sump product of the dissociation apparatus did not become so viscous as a result of resinification as to prevent recirculation.

It will be appreciated that the instant specification and examples are set forth by way of illustration and not limitation and that various modifications and changes may be made without departing from the spirit and scope of the present invention.

What is claimed is:

1. The process for the production of cyclopentadiene by the substantially quantitative splitting or monomerizing of a dicyclopentadiene concentrate containing thermally stable dimers of isoprene and codimers of cyclopentadiene, isoprene and piperylene and having been obtained by the heat treatment of a C₅ fraction of a pyrolysis petrol and its subsequent enrichment by fractional distillation, comprising heating the dicyclopentadiene concentrate in liquid phase in a reactor at a temperature of about 170° to 250° C., and maintaining a concentration of about 10 to 70 percent by weight for the thermally stable dimers of isoprene and codimers of cyclopentadiene, isoprene and piperylene in the reactor.

2. A process as claimed in claim 1 wherein the dicyclopentadiene is continuously supplied, cyclopentadiene is continuously boiled off from the reactor and a portion of the bottoms product in the reactor is continuously withdrawn in such a quantity that the concentration of the cyclopentadiene polymers in the reactor is at most about 50 percent.

3. A process as claimed in claim 2, wherein the withdrawn bottoms product is separated by distillation into a head product containing the thermally stable dimers and codimers and a sump product comprising cyclopentadiene polymers.

4. A process as claimed in claim 3, wherein the thermally stable dimers and codimers obtained as a head product by the distillation of the bottoms product are recycled at least in part to the reactor.

5. A process as claimed in claim 3, wherein a thin-film evaporator is used for the distillation of the withdrawn bottoms product.

6. A process as claimed in claim 1, wherein the residence time of the dicyclopentadiene concentrate in the reactor is less than about 5 hours.

7. A process as claimed in claim 1, wherein heating is effected at a rate to convert more than 90 percent of the dicyclopentadiene in the concentrate to cyclopentadiene.

8. A process as claimed in claim 1, wherein the monomerization of dicyclopentadiene is carried out at atmospheric pressure, reduced pressure or slightly excess pressure.

* * * * *